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16. ABSTRACT

The application of matrix isolation techniques to the infrared spectrometric analysis of organic compounds is reviewed. Literature covered was published during the period from mid-1981 to mid-1988. Analytical applications of gas chromatography/matrix isolation Fourier transform infrared spectrometry are discussed extensively.

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Recent Advances in the Matrix Isolation Infrared Spectrometry of Organic Compounds

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I. SCOPE OF THIS REVIEW

Matrix isolation (MI) techniques have been employed extensively in the past three decades to enable the spectroscopic detection of both inorganic and organic chemical species that are too reactive, too unstable, too rare, or too transient to be studied under ordinary laboratory conditions. However, the application of matrix isolation methods to the study of stable organic species is relatively recent. In this review we primarily address the latter application and emphasize work that has appeared in the scientific literature from mid-1981 to mid-1988. We occasionally refer to the earlier literature to provide a historical perspective from which to assess the current trends. Our treatment of the more familiar, more voluminous, and more extensively reviewed matrix isolation infrared (MI-IR) studies of transient species is not intended to be comprehensive, because much of that work has been discussed elsewhere. Thus, we have provided only a sampling of work in that area as it relates to our discussion of MI techniques for stable organic species.

II. HISTORICAL PERSPECTIVE

The vast majority of the papers in the literature that deal with MI-IR spectrometry report studies of chemical species that are transient or nonexistent at ambient temperatures. These species include free radicals, molecular ions, charge-transfer complexes, and many photolysis and pyrolysis products.

To stabilize these transient species for leisurely spectroscopic examination, use of a low-temperature solvent matrix was proposed and employed by Lewis and Bigeleisen [1] in the early 1940s. These authors used such a matrix to study the visible spectra of the stabilized free radicals produced in the photooxidation of aminobenzenes and aminobiphenyls. Later, in 1954, Norman and Porter [2] used MI to study the radicals formed on photolytic dissociation of ethyl iodide, carbon disulfide, chlorine dioxide, and benzylic compounds in several low-temperature solvent glasses. These authors suggested the use of MI to observe the IR spectra of radicals.

Independently and also in 1954, Whittle et al. [3] introduced the description of matrix isolation used now, which confines its meaning to studies of species trapped at very low temperatures (4 to 20 K) in inert or noble gas hosts such as argon or nitrogen. With these matrix hosts, most reactions of trapped species with the matrix can be avoided, optically transparent matrices can be obtained, and spectral interferences by the matrix in the IR region between 10,000 and 200 cm^{-1} can be eliminated. The authors also anticipated widespread future application of MI techniques to the examination of active species. In 1958, Brown and Pimentel [4] were the first to positively identify a transient species by MI-IR spectrometry.

Bass and Broida [5] reviewed the early work on matrix isolation of transient species in their book on the formation and trapping of free radicals. In the mid-1960s, cryogenic coolers and liquid helium became available commercially, a development that allowed the subsequent rapid expansion of the field of MI spectroscopy.

A critical review of papers up to 1969 is provided in the book on low-temperature spectroscopy by Meyer [6]. This book includes detailed discussions of experimental techniques for MI, characteristics of organic and inorganic glasses appropriate for matrix formation, and procedures for safe handling of cryogenic equipment and other low-temperature experimental apparatus. In addition, it includes extensive vibrational frequency tables for a large number of inorganic species and a few simple organic species isolated in nitrogen or argon matrices.

Work in MI-IR spectrometry published from about 1962 to 1973 is covered in a comprehensive survey by Hallam [7]. Chadwick [8] reviewed the general field of MI spectrometry through 1977 and provided extensive tables outlining the species studied, spectroscopic methods used, and principal findings of each study. Jacox [9] reviewed applications of MI to the study of transient species, not necessarily involving IR spectroscopy, in the same time period.

In 1978, Green and Reedy [10] provided a thorough, critical review of applications of MI techniques combined with Fourier transform infrared (FTIR) spectrometry through mid-1976. These MI-FTIR applications

were primarily related to the study of transient species. At that time, a large body of work existed treating the MI-FTIR characterization of inorganic species; however, few applications of MI-FTIR to organic species had been reported, except for the analysis of radicals formed from the photolysis of simple organic compounds, such as allene, methylacetylene, and dicyanoazomethane, and stable compounds in the class of polynuclear aromatic hydrocarbons (PAHs). The application of MI-FTIR to the analysis of PAHs is discussed in Section IV of this review.

Barnes and Orville-Thomas [11] also reviewed MI-FTIR applications to the study of transient species. Applications of MI to organic chemistry were reviewed by Dunkin [12], who noted that by 1980, MI could be considered to be a well-established technique, ready for use in an expanded variety of areas of general interest to chemists.

Matrix isolation spectroscopy and advances within this field through 1980 are covered in a book by Barnes et al. [13]. Contributions by a number of authors describe applications of MI spectroscopy to the investigation of transient species, both organic and inorganic; the generation and trapping of unstable solutes; the characterization of stable molecules; the study of relaxation and energy transfer processes; the determination of conformational isomerism; and the investigation of matrix effects. In addition to MI-FTIR methods, other spectroscopic techniques, such as electron spin resonance and Mössbauer effects, were addressed.

Andrews [14] in 1980 reviewed the literature concerning the spectroscopy of molecular ions isolated in noble gas matrices. Applications of MI-FTIR spectrometry and other forms of spectroscopy in combination with MI techniques were described. Most of the applications reviewed by Andrews were to inorganic species and some halogenated methanes.

III. TRANSIENT SPECIES

By far the greatest number of published works on MI-IR spectrometry addresses measurements on free radicals and other transient species. Because this area of research is large and has been extensively reviewed, we present only a selection of recent works dealing with the MI-IR spectrometry of transient species. Works that are cited in several areas, including free radicals, hydrogen bonding, conformational analysis, unstable reaction products and intermediates, and pyrolysis products, illustrate the current status of MI-FTIR of transient species.

A. Free Radicals

Andrews [15] briefly reviewed several studies involving IR and Raman spectroscopic measurements of transient species produced during chemical reactions and trapped at 15 K in an argon matrix. Most of the studies concerned inorganic species. However, Andrews also reported the IR spectra of free radicals produced by halogen abstraction and of halomethyl cations produced by photolysis and radiolysis. Applications of MI-FTIR to the measurement of free radical species are described in a symposium volume published in 1986 [16].

In a series of papers, Ase et al. [17], Chettur and Snelson [18-20], and Cyvin et al. [21] described in detail the use of MI-FTIR for characterizing primary, secondary, and tertiary alkylperoxy and alkyl radicals isolated in either argon or argon and oxygen matrices. These researchers reported the MI-FTIR spectra of peroxymethyl (CH_3O_2) and its dimer ($CH_3O_4CH_3$), which is chemically bonded through an oxygen chain; the ultraviolet (UV) photolysis of CH_3O_2 in an argon-oxygen matrix [17]; and the normal coordinate analysis of CH_3O_2 and several related isotopic species [21]. Similar studies of peroxyisopropyl ($i\text{-}C_3H_7O_2$) and isopropyl ($i\text{-}C_3H_7$) radicals were described by Chettur and Snelson [18]. The work has since been extended to peroxyethyl ($C_2H_5O_2$) and ethyl (C_2H_5) radicals [19] and the $t\text{-}C_4H_9O_3$ radical [20]. For further references on MI-FTIR studies of free radicals, the above papers and reviews should be consulted.

B. Hydrogen Bonding and Complexes

The use of MI-FTIR to study systems capable of hydrogen bonding was reviewed by Perchard [22] in 1981. If the hydrogen bond energy is relatively small, less than approximately 50 kJ/mol, the IR absorbances of successive monomers, dimers, trimers, and further polymers of self-associated compounds can be observed by starting from high matrix to solute (M/S) ratios and then progressively increasing the concentration of solute. Because the bandwidth of the proton-donor-group stretching absorption is greatly narrowed under MI conditions, the causes of band broadening and the mechanisms that produce multiplet structures can be studied. For hydrogen-bonded complexes between unlike species, MI offers the unique possibility of observing the isolated 1:1 complex in an inert medium and in the ground state. In the case of strong hydrogen bonds, this can allow identification of intermediate states in which the proton is shared, rather than transferred, between acceptors.

Applications of MI-FTIR spectrometry to the study of hydrogen-bonded solids, as well as amide group planarity and conformational

analysis, were illustrated in a brief review by Van der Veken [23]. Even though the monomers of many compounds have been observed in the gas phase at elevated temperatures, detailed analysis of the spectra is often difficult because of the broadness of the vibrational bands. Impurities from gas-phase decomposition products may also confound the problem. Thus the narrow bandwidths and low reactivity inherent in MI-FTIR spectrometry provide an excellent opportunity for the study of such compounds.

Matrix-isolated monomeric and dimeric hydrogen sulfide were studied in inert argon matrices by Barnes and Howells [24] and Agarwal et al. [25], but uncertainties existed in the IR assignments of the fundamental H_2S absorptions. Recently, Woodbridge et al. [26] studied the photooxidation of hydrogen sulfide in a solid oxygen matrix. Although the ν_1 H−S stretching absorption of the monomer was too weak to be observed, the ν_3 absorption at 2635.0 cm^{-1} was identified. The observed hydrogen-bonding dimer frequency, which was shifted 50 cm^{-1} to lower energy relative to ν_3 of the monomer, was in agreement with calculated values from ab initio molecular orbital calculations.

Andrews et al. [27] examined complexes of acetylene and hydrogen fluoride in argon matrices at 20 K; and later, Johnson and Andrews similarly examined hydrogen cyanide:HF [28] and acetonitrile:HF [29] complexes. Although the MI-FTIR results showed that hydrogen bonding in acetylene occurs to the π-electron system, hydrogen bonding in HCN and in acetonitrile occurs to the lone pair electrons of the nitrile nitrogen. Warming of the 1:1 acetonitrile:HF complex in the matrix to temperatures greater than 20 K resulted in diffusion of HF through the matrix and formation of complexes having two or three molecules of HF bound to one acetonitrile molecule.

In these studies, evidence was obtained by Johnson and Andrews [28] for the presence of two distinct 1:1 complexes of HCN with HF in argon at 12 K: HF:HCN and HCN:HF. The concentration of the former decreased on warming at temperatures greater than 20 K, whereas the concentration of the latter increased, indicating that HCN:HF is the more stable of the two complexes. This relatively more stable complex exhibited only a single degenerate librational mode at 585.8 cm^{-1}, which led the authors to characterize it as linear. A nonlinear structure for the less stable complex was indicated by the doublet structure of its C−H bending mode. An interesting aspect of these studies is that MI allowed observation of the less stable complex, which could not be observed in vapor-phase studies.

In addition to the complexes of acetylenic and nitrilic compounds described above, the structure and bonding of ammonia:HF complexes were examined by Andrews [30] and Johnson and Andrews [31]; the

structure and bonding of HF complexes with the two homologous series of methylamines and ethylamines, plus piperidine, were examined by Andrews et al. [32]. The NH_3:HF complex exhibited a strong hydrogen bond, with C_{3v} symmetry. Distinct 1:1 and 1:2 complexes were formed, with either one or two molecules of HF bound to each of the amines. In the amine complexes, splitting of the ν_1 absorption from librational motions of the HF moiety resulted from the reduced symmetry at the amine nitrogen when hydrogen bonding occurred to the amine lone pair electrons. Increased methyl substitution resulted in stronger acid-base interactions and increased yields of the 1:2 complexes. Although very strong hydrogen bonds in the trimethylamine:$(HF)_2$ complex are indicated by its MI-FTIR spectrum, the proton closest to the amine is shared by both the amine and the nearest fluorine. The proton of the second HF molecule is hydrogen-bonded to the fluorine of the first HF, but remains closer to the fluorine of the second HF.

Hunt and Andrews [33] then examined the interesting case of cyanamide, H_2NCN, in which hydrogen bonding will be influenced by the competing effects of the electron-donating amino group and the electron-withdrawing nitrile group. Mixtures of hydrogen fluoride and its deuterated isotopomer were co-deposited with cyanamide, cyanamide-d_2, and dimethylcyanamide in argon at 12 K. Cyanamide has three potential bonding sites for the HF in a 1:1 complex: the amine nitrogen lone pair, the nitrile nitrogen lone pair as in HCN and CH_3CN, and the π-electron system as in acetylene. On the basis of the small splitting (8 cm^{-1}) of the ν_1 mode, the authors concluded that in the 1:1 complex the HF hydrogen bonds to the lone pair of the nitrile nitrogen. Methyl substitution on the amine nitrogen did not change this bonding site. The effect of the nitrile group on the amine is to withdraw electron density from the lone pair, thereby decreasing the basicity of the amine group and increasing the basicity of the nitrile group. Therefore, a linear H_2NCN:HF 1:1 complex, similar to that observed with acetonitrile and HF [29], is formed.

Machara and Ault [34] studied the 1:1 complexes formed by ClF with the nitrogen bases ammonia, trimethylamine, acetonitrile, acrylonitrile, and hydrogen cyanide in argon and nitrogen matrices. All the complexes exhibited absorptions at frequencies below 700 cm^{-1}, which were dominated by the red-shifted Cl−F stretching band. Large shifts between spectra obtained in argon and those obtained in nitrogen suggested that the complexes have significant ionic character.

Davis and Andrews [35] used MI techniques to study the IR spectra of complexes of HF with phenylalkynes in nitrogen and argon matrices. Truscott and Ault [36, 37] similarly used MI-FTIR spectrometry to study complexes of cyclic hydrocarbons and various acidic species.

Related works that primarily address MI-FTIR studies of inorganic complexes have also been published. Some recent examples are the work of Withnall and Andrews [38] on hydroxylamine; the work of Lascola et al. [39] on the complexes of HF with HNF_2, NF_3, PF_3, and PCl_3; the work of Andrews et al. [40] on ozone and sulfur dioxide complexes with HF; the work of Andrews and Hunt [41] on carbon monoxide complexes with HF; and the work of Hunt and Andrews [42] on diatomic halogen complexes with HF.

In their study of carbon monoxide complexes with HF, Andrews and Hunt [41] found two 1:1 complexes: OC:HF and CO:HF. The second of these complexes was favored by slow spray-on deposition, indicating that, in agreement with theoretical predictions, it is the less stable of the two. This finding demonstrates that the matrix quenches the internal energy of the molecule fast enough to prevent rearrangement of the less stable complex to the more stable form.

Knözinger and Leutloff [43] examined the MI-FTIR spectra of several polar molecules in argon, krypton, or xenon matrices, and discussed the spectrum of acetonitrile in detail. The far-IR spectrum of matrix-isolated aceonitrile exhibited characteristic absorption patterns at frequencies less than 150 cm^{-1}, which were below the lowest fundamental frequency (370 cm^{-1}) of the monomer. These absorption patterns were characterized as follows: Specific absorption bands below 100 cm^{-1} were assigned to (1) the vibration of the monomer within the polarized cage of the matrix, which was indicated by a decrease in relative intensity of the bands upon annealing or decreasing the M/S ratio, and (2) phonon bands of the solid matrix, which were activated by the polar impurities. The phonon band assignments were based on their similarity to phonon bands observed in the presence of other matrix-isolated species, such as HCl, and were consistent with the small isotopic effect observed on deuteration of the monomer. Two sharp absorption bands between 100 and 150 cm^{-1} were assigned to a dimer with C_{2h} symmetry, in which the two polarized acetonitrile moieties lie side by side. This assignment was supported by an increase in the relative band intensity upon annealing or decreasing the M/S ratio, the determination of the IR-active intermolecular vibrational modes, and the observed isotopic effects on deuteration, which were in agreement with theoretical values for pure rotatory vibrations.

Kvisle and Rytter [44] were able to observe the IR spectra of both dimers and monomers of aluminum alkyls by thermal dissociation of the dimers at relatively high temperatures (573 and 353 K) and isolation of these highly reactive compounds, triethylaluminum and trimethylaluminum, in low-temperature argon matrices. Controlled dimerization of the trimethylaluminum by annealing the matrix indicated that the for-

mation of the dimer proceeds through a singly bridged intermediate. Trimethylgallium, which does not form dimers, was also studied.

C. Matrix Effects and Conformational Isomers

Although the MI techniques used in the last few years have primarily employed condensed inert gas matrices, such as argon or nitrogen, evidence has accumulated that the matrix itself exerts an influence on the MI-FTIR spectra [45-47]. Vibrational frequencies of matrix-isolated species are often shifted from their vapor-phase values. In general, high frequency stretching modes usually shift to lower frequency, and low frequency bending modes usually shift to higher frequency. Several factors may contribute to matrix effects. Multiple trapping sites may produce several vibrational bands; rotation within a site may produce band splitting; aggregation within a site may shift vibrational bands, especially for hydrogen-bonded species; and the presence of the matrix may perturb the solute sufficiently to resolve degenerate or nearly degenerate bands.

Durig and Sullivan [46] reviewed molecular motion (rotation) in matrices. They pointed out that the noble gases form face-centered cubic crystals which have three possible types of sites: (1) tetrahedral or (2) octahedral holes, depending on whether the atomic centers are equidistant from four or six atoms, or (3) substitutional holes, where one atom is removed from a lattice site. Each site may give a unique matrix-solute interaction. Fine structure from hindered rotation of the solute may occur in symmetrical sites. The authors provided a table of site diameters and characteristics for four noble gases appropriate for MI experiments.

The vibrational bands of conformers often differ by only a few wavenumbers. Hence these bands may not be resolvable at ambient temperatures. However, in MI spectroscopy of the same species, the bandwidths are considerably reduced, and the spectra of the separate conformers can often be distinguished. Barnes [48, 49] reviewed the literature addressing this topic, which includes studies of several haloalkanes, alkenes, alcohols, esters, and nitrites.

In work by Charles et al. [50] and by Fan and Boggs [51], the IR spectra of the cis and trans conformers of acrylic acid, formed by UV irradiation of the matrix-isolated monomer at 25 K, were observed. Comparison of the observed spectra with the results of theoretical calculations allowed assignments of the observed absorptions to normal vibrational modes of the two conformers.

Fisher and Michl [52] were able to observe the less stable of the two conformers of 1,3-butadiene by depositing the sample in an argon

matrix at 10 K directly from an oven held at 1200 K, thus trapping the high-temperature equilibrium mixture. Irradiation with linearly polarized light produced photoselection and partially oriented solid solutions of the conformers. From the IR transition-moment directions, the authors deduced that the less stable conformer has C_{2v} symmetry, and thus has a planar s-cis structure.

The vibrational spectra and conformational behavior of dimethylsulfite were recently studied by Barnes and Van der Veken [53].

Studies of conformational isomers by MI-FTIR have generally included the implicit assumptions that (1) the conformational equilibrium that existed under the conditions prior to deposition still exists in the matrix-isolated phase and (2) interconversion of conformers does not occur under MI conditions. However, in a few cases these assumptions have been shown not to be valid [54-59], particularly when the matrix is annealed at 35-40 K. Barnes [48] correlated the data from these works to generalize the conditions under which conformational interconversion may occur in the matrix at 20 K. If the barrier to rotation is less than 6 kJ/mol (1.4 kcal/mol), a molecule will be in conformational equilibrium in the matrix. If the barrier is less than about 12 kJ/mol, annealing at 35-40 K will result in loss of the less stable conformer. Serrallach and Meyer [55] reported that the history of the matrix, for example, the deposition conditions and the highest temperature reached, may have a profound effect on the reversibility of conformer interconversion.

Barnes [48, 49] points out the difficulty of separating conformational splittings from those resulting from interactions with the matrix itself and suggests means to distinguish them. Doublet or multiplet structure that results from rotation or libration of the solute in the matrix has been shown to occur only with very small molecules, such as water or hydrogen chloride, and can usually be discounted for the larger compounds expected to show conformational isomerism. Splittings that arise from the aggregation of molecules in the matrix can be eliminated by increasing the M/S ratio until no further changes with concentration occur. Band splitting that results from multiple trapping sites will be independent of the concentration, as is conformational isomerism; thus the best diagnostic test for multiple trapping sites is the use of another matrix which would be unlikely to exhibit the same number and types of trapping sites. Confusing additional bands that arise from impurities in the matrix and that may be mistaken for conformationally induced multiplet structures can be eliminated by purifying the matrix gas and solutes prior to deposition.

D. Reactive Intermediates and Reaction Products

The low temperatures at which MI spectra are obtained allow examination of reaction products and intermediates that are unstable at ambient temperatures. Snelson [60] has reviewed applications of MI-FTIR spectrometry to the study of high-temperature vapors, such as pyrolysis products produced in a furnace. Through MI techniques, the IR spectra of species that have vapor pressures ranging from 10^{-4} to 10^{-5} atm (10^{-2} to 10^{-3} kPa) at temperatures less than 2800 K can be readily obtained, and containment problems are greatly reduced.

A recent paper by Shepherd and Graham [61] illustrates the application of MI-FTIR to the characterization of high-temperature vapors. Silicon carbide was vaporized at 2900 K, and the products were quenched in argon at 8 K. Various geometries were assumed for the vaporization product, SiC_2, and its ^{13}C isotopically substituted counterparts. The MI-FTIR spectra showed that SiC_2 is cyclic, with C_{2v} symmetry in the ground state. This is in contrast with previous assumptions of a linear molecular geometry, but in agreement with a previously published rotational analysis of the SiC_2 band at 500 nm.

Products of the pyrolysis of coal have been studied by MI-FTIR spectrometry in work reported by Margrave and Hauge [62] and Chu et al. [63]. Gaseous products and intermediate species were trapped in an argon matrix at 15 K. A metastable intermediate that is a potential precursor to tar formation was observed, and the conditions leading to its formation were investigated, but this intermediate was not fully characterized [62]. Several gaseous species and possibly free radicals were identified [63].

Co-condensation reactions of metal atoms with molecules and the products of these reactions have been studied extensively in the past by MI techniques. This topic was reviewed by Moskovits and Ozin [64] and Andrews [65, 66]. Many of the studies employed primarily Raman spectroscopy; however, MI-FTIR spectrometry was also used, mainly for examining inorganic species. Some recent examples of applications to metal atom–inorganic molecule reactions are described in works by Mascetti and Tranquille [67] and by Ayed et al. [68]. Some applications to organic species are described below.

Manceron and Andrews [69] used MI-FTIR spectrometry to examine the complexes formed by the co-condensation of lithium atoms with phenylacetylene or styrene in an argon matrix. Complexes having one lithium atom and either one or two organic ligands were formed. For the lithium:phenylacetylene complex, two structural isomers were observed, one with the lithium bound to the triply bonded ethynyl group and the other with the lithium bound to the arene moiety. These isomers

could be interconverted photochemically in the matrix. Styrene formed similar complexes with the arene or with the vinyl moieties, but no photochemical interconversion was observed. The di-ligand species was shown to have a sandwich structure.

Reactions between atomic nickel and acetylene in argon matrices at 12 K were studied by Kline et al. [70]. At very low concentrations of nickel, a π-complex between the nickel and the acetylene triple bond was formed. Irradiation of the complex with visible light caused rearrangement to form nickel vinylidene, $NiCCH_2$. When higher concentrations of nickel were used, a dinickel acetylene π-complex was formed. This dinickel complex did not, however, rearrange photochemically.

Metal-carbene complexes have been suggested as intermediates in several catalytic processes, such as the copper-catalyzed decomposition of diazo compounds, but until a recent series of investigations by Chang et al. [71, 72], no spectroscopic evidence for their existence had been reported. These researchers set out to examine systematically the matrix-isolated reactions of the first-row transition metals with diazomethane. In the first of these studies [71], they found that atomic iron and diazomethane react spontaneously in both argon and nitrogen matrices and form the simple species $FeCH_2$. Recently, Chang et al. [72] extended this study to the reaction of copper atoms and diazomethane. In a contemporaneous study by Hauge et al. [73], copper atoms were vaporized in a furnace at approximately 1500 K and cocondensed with diazomethane and argon on a cryogenic surface at 11 to 14 K for MI-FTIR measurements. Concentration variation studies allowed determination of the reaction stoichiometries, and assignments were confirmed by use of isotopically substituted reactants. Spontaneous reaction between copper and diazomethane occurred. Selected wavelength photolysis of the matrix-isolated species in argon allowed identification of $CuCH_2$, N_2CuCH_2, and a copper-diazomethane adduct, $Cu(CH_2N_2)$; the N_2CuCH_2 could be photolytically dissociated and reassociated at appropriate wavelengths. In nitrogen matrices, significant frequency shifts from those in argon were observed, and N_2CuCH_2 and $Cu(CH_2N_2)$ were again formed. However, the former species could not be photolytically dissociated when in nitrogen. At high copper concentrations (0.86 and 1.41% Cu) and an initial concentration of 1.27% diazomethane in argon, evidence of dicopper or larger copper cluster products was observed. Because the IR absorptions of the copper insertion products and N_2CuCH_2 were similar in both argon and nitrogen, the authors suggested that only one N_2 molecule significantly interacts with $CuCH_2$ in the nitrogen matrix.

IV. STABLE SPECIES

A. Chemical Characterization Studies

Turner [74] reviewed MI-FTIR spectrometry of stable molecules in 1981 and discussed several techniques for producing stable matrices that had been used up to that time: slow spray-on deposition (SSO), pulsed deposition (PD), and freezing from a noble gas solution. He pointed out that, as demonstrated by the work of Rochkind [75, 76] and Perutz and Turner [77], PD was generally shown to be quicker and to result in fewer impurities in the matrix.

Several early studies utilized MI techniques to examine the IR spectra of gaseous species. The work of Rochkind [75, 76, 78, 79] is especially illuminating. The first use of MI-FTIR for characterizing mixtures of stable organic species was published by Rochkind in 1967 [75]. To overcome the unpredictable IR frequency shifts that could be expected in a cryogenic, but not matrix-isolated environment, Rochkind adapted MI techniques to his work. He then demonstrated the qualitative and quantitative analyses of a mixture of 13 C-1 to C-4 hydrocarbons by PD-MI-FTIR. The spectra exhibited a small number of well-defined frequencies for each of the compounds. Fundamental frequencies differed by less than 0.5% from the gas-phase values, although the M/S ratio employed by Rochkind (100/1) was near the lower limit necessary to achieve matrix isolation, which led him to term his use of MI techniques "pseudo-matrix isolation." Although frequencies, bandwidths, and relative intensities were reproducible, Rochkind cautioned that absolute intensities might not be reproducible with MI-IR techniques and therefore advised the use of internal standards for quantification. In the following year, Rochkind published [76] analyses of mixtures of isotopically labeled gases and demonstrated that MI-FTIR spectrometry is superior to gas chromatographic methods for the qualitative analysis of isotopic molecules. The remarkable selectivity of MI-FTIR was exhibited by the spectrometric separation of the three isomers of ethylene-d_2. Qualitative and quantitative analyses of several isotopically labeled gases, for example, deuterated methanes, ethylenes, methyl ether, propionaldehyde, and neopentane, were performed.

In 1970, Rochkind [79] published a catalog containing MI-FTIR spectra of 89 organic compounds obtained in the analyses of gas mixtures by the method discussed above. Beer's law was shown to be obeyed over a wide concentration range. In a seminal summary paper [78], Rochkind demonstrated more conclusively that MI-FTIR can be appropriately used for quantitative determinations. Therein he also predicted the future use of gas chromatography (GC) combined with MI-FTIR spectrometry.

More recently, Griffith and Schuster [80] measured several trace gases in the atmosphere at ground level and from an aircraft between 9 and 14 km above ground level. The samples were collected in a solid matrix of atmospheric carbon dioxide at 77 K by drawing air through a coiled glass tube that was cooled by liquid nitrogen. After vacuum sublimation of the sample and removal of water, a matrix of CO_2 was grown by PD for MI-FTIR analysis. Peroxyacetyl nitrate (PAN) and several inorganic species were identified and quantified. Detection limits were in the range of 3 to 300 ppt in air.

Purnell et al. [81] used both SSO and PD to examine the MI-FTIR spectra of some low-molecular-weight amines. They found that Beer's law was obeyed at an M/S ratio of about 100. Anomalous intensity variations in the NH_2 wagging absorption of methylamine in a nitrogen matrix were attributed to differing orientations of the nitrogen molecules in the matrix. In an argon matrix, this absorption had a complex structure, which the authors attributed to differing matrix sites. Ball and Purnell [82] examined mixtures of low-molecular-weight amines by using PD of a mixture of nitrogen and amines onto a cryogenic surface. The simplified spectra obtained with MI enabled identification of the various compounds, which are difficult to separate by GC. Beer's law was obeyed overall, with the exception of the anomalous band of methylamine discussed above.

The dispersive IR spectra of benzene in argon and krypton matrices were studied by Brown and Person [83]. The spectra were strongly affected by aggregation of benzene molecules in an argon matrix; an M/S ratio of at least 3000 was necessary to isolate benzene effectively in argon. Although the relative intensities were consistent between the MI and vapor-phase spectra, the absolute intensities were not. This inconsistency again points to the need to use well-characterized internal standards for good quantification in MI-IR analyses.

George et al. [84] analyzed the MI-FTIR spectra of monomeric and polymeric forms of acrylonitrile to characterize the out-of-plane olefinic CH deformation vibrations. This work demonstrated that SSO matrix deposition is preferable to PD for the avoidance of polymer formation in compounds of this type.

In a preliminary presentation, Presser et al. [85] reported the observation of small positional shifts in the 2700-3000 cm^{-1} region that reflected the isomerism of 2- and 3-methylpentane.

B. Analytical Applications

The recent expansion of the analytical application of MI-IR spectrometry to stable organic compounds has been facilitated by the high

signal-to-noise (S/N) ratio and frequency accuracy made possible by FTIR instruments. In a review covering the scientific literature through early 1982, Mamantov et al. [86] discussed analytical applications of MI-FTIR and GC/MI-FTIR and delineated the requirements that must be met by a spectroscopic method for analytical applications: (1) The spectra of individual molecules must have narrow bandwidths and high resolution. (2) The spectrum of an individual molecule must be unique, unambiguous, and relatively simple. (3) The spectral features for a given compound must be reproducible from sample to sample. (4) The molar absorptivity of a compound must be independent of concentration and not be affected significantly by other sample constituents. (5) The sampling medium must be transparent, inert, and chemically pure. (6) The sample must be soluble in the medium.

These authors then illustrated the adherence of MI-FTIR spectrometry to the above requirements with examples from their own work and the recent literature. They confirmed [87], in a study of polynuclear aromatic hydrocarbons, that the use of an internal standard greatly improves quantification. We discuss several of these illustrations later in this section.

Wehry and Mamantov [88] recently updated their coverage of the literature through early 1987 in a review of analytical applications of MI molecular spectrometry which includes MI, GC/MI-FTIR, and MI-fluorescence (MI-F).

1. Characterization of Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons constitute a significant fraction of airborne particulate matter. Several PAHs have been shown to be carcinogenic or mutagenic, and most PAH isomers exhibit vastly different biological activity. The ability to identify each isomer is therefore important. However, analyses for PAHs are complicated by the difficulty in separating many of the isomers by GC and the inability to distinguish them by gas chromatography/mass spectrometry (GC/MS). In addition, poor sensitivity has historically limited the use of IR spectrometry in the characterization of PAHs. This limitation is compounded by the weak IR absorbance exhibited by PAH compounds. However, the development of Fourier transform methods and more sophisticated sampling techniques, such as matrix isolation, has facilitated the analysis of PAHs by IR spectrometry. Wehry, Mamantov, and coworkers have published a series of articles describing the use of MI-FTIR for the characterization of PAHs in complex samples [89-98].

In 1976, Wehry et al. [89] first illustrated the use of MI-FTIR for the analysis of PAHs. The initial problem with examining PAHs by MI techniques is volatilization of the compounds so that they can be mixed

with the matrix gas. Because PAHs are readily vacuum-sublimed, Knudsen effusion was used to prepare the matrix-isolated samples. With this deposition technique, submilligram amounts of solid samples can be analyzed. A disadvantage of the Knudsen effusion technique is that deposition is relatively slow; approximately 2 h are required to obtain a good matrix deposit. Another disadvantage is that different compounds sublime at different temperatures. Therefore, compounds in a mixture that have dissimilar vapor pressures cannot be deposited simultaneously by using one cell temperature. However, as demonstrated later by these workers [96], this is fortuitous in that samples can be fractionated by careful control of the Knudsen cell temperature. The authors [89] found that nitrogen is a suitable matrix gas for the analysis of PAHs and demonstrated that the positions of the IR bands for any one matrix-isolated compound were independent of the presence of other components in the sample. As shown in Fig. 1, the uniqueness of the MI-FTIR spectra of individual PAHs enabled the identification of specific PAHs in a four-component mixture.

In a continuation of work by the same group, Mamantov et al. [90] examined the MI-FTIR spectra of several PAHs. These spectra exhibited absorption maxima between 900 and 700 cm^{-1} and were sufficiently different in that spectral region to allow the unambiguous identification of specific PAHs in mixtures of up to 10 PAHs. An increase in the M/S ratio resulted in a decrease in bandwidths; some peaks that originally appeared as singlets were resolved into doublets. Detection limits, based on a S/N ratio of 2 for absorbance, were less than 1 μg for typical PAHs. For example, a detection limit of 0.5 μg was achieved for perylene. Absorbance maxima for nine replicate depositions of pyrene exhibited a relative standard deviation of 15.3%. The relative standard deviation improved to 10.4% when the matrix was annealed at 25 K for 30 min. Annealing at low solute levels sometimes resulted in a decrease in bandwidth and an increase in absorbance, although these effects were not well understood. Pulsed deposition, as opposed to the continuous deposition primarily used in this study, offered a small saving in time but resulted in poorer isolation of PAH molecules in the matrix. After comparing matrix isolation to other more conventional IR sampling techniques, such as incorporating the analyte in KBr pellets or using attenuated total reflectance (ATR), the authors concluded that (1) Beer's law is obeyed over a larger concentration range for the MI technique than that for KBr pellets or ATR and has a range similar to that for liquid solutions, (2) detection limits are equivalent or superior to the conventional IR sampling techniques, and (3) bandwidths obtained in annealed nitrogen matrices are narrower than those in conventional IR matrices, such as KBr.

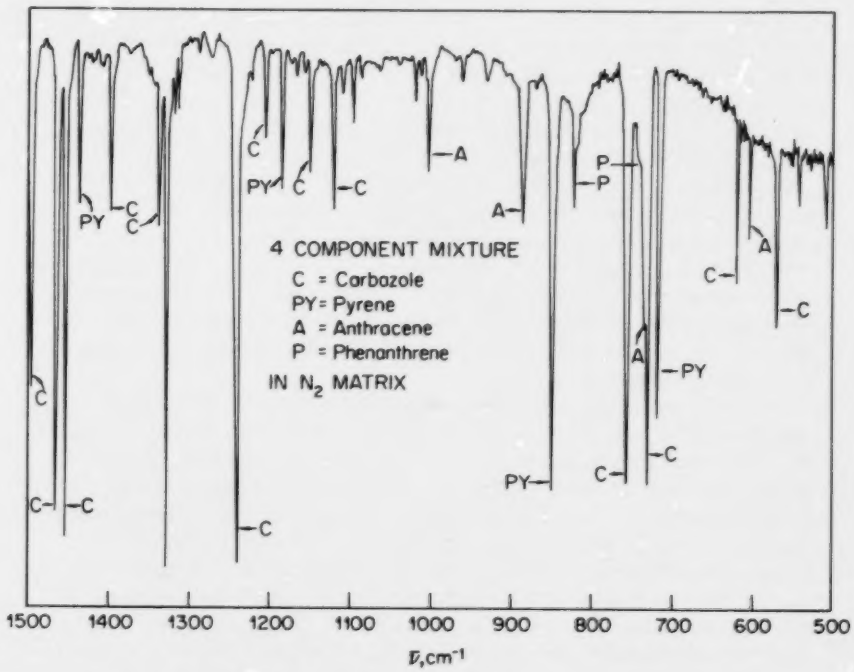


FIG. 1. Spectrum of a four-component PAH mixture co-deposited with nitrogen; 100 scans at 2 cm^{-1} resolution. Reprinted from Ref. 89. Copyright 1976 by Raven Press.

The MI-FTIR spectra of the six monomethylchrysene isomers were examined by Tokousbalides et al. [91]. All six isomers exhibited distinct differences in the 900-700 cm^{-1} spectral region. Four of the six isomers were unambiguously identified by MI-FTIR in a six-component mixture, whereas the spectra of 4- and 6-methylchrysene did not exhibit enough unique features to allow clear identification of each isomer. Beer's law plots for individual methylchrysenes were linear over a wide concentration range, from the detection limit of 0.2 to 5.0 μg. The authors [91] also illustrated the complementarity of MI-FTIR and MI-F spectrometries for the characterization of PAHs.

Wehry et al. [92] presented an overview of the analysis of PAHs by MI-F and MI-FTIR spectrometries. The authors noted that, although IR methods are not as sensitive as fluorescence techniques, IR spectra

are much more useful for the identification of unknowns. Many of the difficulties associated with IR sample preparation are alleviated by MI techniques. The proper choice of matrix gas ensures transparency of the matrix throughout the IR spectral range, a feature that is not characteristic of salt pellets, solutions, and mulls. Uniform dispersion of the solute in the matrix, which is difficult for samples in mulls or salt pellets, is readily attained under typical MI conditions. As a result, Beer's law is obeyed over a wider range of concentrations, with a linear dynamic range of three decades in PAH concentrations. The practical aspects of MI-FTIR spectrometry for the characterization of PAHs were illustrated by analyzing a three-component mixture of the isomers benz[a]anthracene, chrysene, and triphenylene. Each PAH isomer was identified by comparison of specific bands in the mixture to standard reference spectra.

Mamantov et al. [93] used liquid chromatography (LC), MI-FTIR spectrometry, and MI-F spectrometry to identify and quantify specific PAHs in coal liquids and shale oils. The authors noted that these particular samples were too complex to be characterized by a single analytical technique. Therefore, PAHs in the mixtures were separated by LC into fractions determined primarily by the number of aromatic rings. The separated fractions were then analyzed by MI-FTIR and MI-F. Several PAHs, including pyrene, chrysene, benz[a]anthracene, and benzo[a]pyrene, were identified in these fractions. However, the presence of aliphatic hydrocarbons in the fractions interfered with the MI-FTIR identification of specific PAHs. Thus, the authors concluded that examination of these samples by MI-FTIR would require a pretreatment step to remove the aliphatics. Nevertheless, the combined MI-FTIR and MI-F analyses of the coal liquid and shale oil showed that both oils contained significant concentrations of benzo[a]pyrene, nearly 2 ppm in the shale oil sample, and were rich in pyrene. In general, the quantitative results from MI-FTIR and MI-F were in good agreement.

Microsampling procedures for the quantitative analysis of PAHs by MI-FTIR spectrometry were reported by Hembree et al. [94]. Two separate systems, a microsampling and an ultramicrosampling system, were described. The ultramicrosampling apparatus used a 6X beam condenser to reduce the diameter of the IR beam from 25 mm to approximately 4 mm at the beam focus. Use of this optical system required a more compact cryostat head design and a smaller Knudsen cell. To prevent the premature sublimation of volatile compounds, such as naphthalene derivatives, upon evacuation of the cryostat head, a cooled Knudsen cell was developed in which the sample was maintained at subambient temperatures until it was deposited. The cooled Knudsen cell was used for the qualitative analysis of a series of dimethylnaphthalenes

and the quantitative analysis of biphenyl; naphthalene was used as the internal standard. In general, detection limits for PAHs were reduced by a factor of 5 to 10 by using the ultramicrosampling apparatus; these detection limits ranged from 50 to 500 ng.

Hinton et al. [95] examined the MI-FTIR spectra of several isomeric methylnaphthalenes and methylbiphenyls. They found that the MI-FTIR spectra of naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 3-methylnaphthalene, and five dimethylnaphthalenes were sufficiently different to allow unambiguous identification of the individual isomers in mixtures. A Beer's law plot for naphthalene in a mixture containing 25 μg each of 1- and 2-methylnaphthalene was linear from the detection limit of 500 ng to 100 μg. The MI-FTIR spectra of biphenyl and 2-, 3-, and 4-methylbiphenyl also allowed the identification of each compound in a mixture. A calibration curve for biphenyl, based on analyses using naphthalene as an internal standard, was linear from 300 ng to 5 μg. Detection limits for the methylbiphenyls were also approximately 300 ng.

To achieve limited fractionation of complex mixtures during MI sample deposition, Wehry et al. [96] used variable-temperature vacuum sublimation to analyze a five-component mixture of PAHs. The mixture was analyzed by first heating the Knudsen cell to a temperature range between 298 and 348 K. After a second surface was positioned for sample deposition, the cell was heated to a range between 348 and 473 K. Analysis of the two fractions by MI-FTIR revealed that phenanthrene, fluoranthene, and pyrene were in the first fraction and that the less volatile compounds, perylene and chrysene, were in the second fraction. The fractional sublimation procedure was used to analyze an adsorption chromatography fraction from a coking plant wastewater stream. Phenanthrene, anthracene, fluoranthene, and pyrene were identified in the low-temperature fraction; and fluoranthene, pyrene, benz[a]anthracene, chrysene, and benzo[a]pyrene were identified in the high temperature fraction.

Garrison et al. [97] applied MI-FTIR to qualitative and quantitative analysis of nitrogen- and oxygen-containing PAHs. The MI-FTIR spectra of several heterocycles, including pyrrole, carbazole, pyridine, acridine, aniline, and several indoles, quinolines, and phenols, were examined. For nitrogen-containing aromatic compounds, the 1500-1200 cm^{-1} spectral region containing the ring-stretching modes was found to be the most useful for distinguishing closely related compounds. Special attention was given to quinoline derivatives in this study. Quinoline and isoquinoline, which differ only by the position of the nitrogen atom in the aromatic ring, exhibited distinct MI-FTIR spectra. This enabled simultaneous analysis of the two isomeric compounds. Four

dimethylquinolines could also be distinguished by their MI-FTIR spectra. The effect of the nitrogen atom on the central aromatic ring was examined by comparing spectra of acridine (one nitrogen heteroatom), phenazine (two nitrogen heteroatoms), and anthracene (the parent PAH). In general, the C−H out-of-plane bending modes were very similar for these compounds. However, substitution of a nitrogen atom for one of the carbon atoms on the central aromatic ring shifted the C−H out-of-plane deformation to higher energy. The compounds could be clearly distinguished by differences in the ring-stretching modes at frequencies greater than 1100 cm^{-1}. This study demonstrated the use of MI-FTIR for the discrimination of a variety of polar aromatic compounds.

In a more recent study, Stout and Mamantov [98] obtained MI-FTIR spectra of 12 nitro-PAHs. The MI-FTIR spectra of nitro-PAHs characteristically exhibit strong absorptions due to either the symmetric or asymmetric stretching vibrations of the nitro group in the 1565-1500 cm^{-1} region. The most useful spectral region for distinguishing individual nitro-PAHs was between 1000 and 650 cm^{-1}, which contains the C−N stretching and C−H out-of-plane bending modes. Individual nitro-PAHs were identified in mixtures containing five different nitro-PAHs. The ability of MI-FTIR to discriminate between isomeric compounds of this type was demonstrated by examining a three-component mixture of dinitropyrenes. Unique spectral features in the 950-750 cm^{-1} region of the MI-FTIR spectrum of the mixture could be assigned to each specific isomer. With pyrene used as an internal standard, a Beer's law plot for 1-nitropyrene was linear over two decades and had a correlation coefficient of 0.999.

2. Development of GC/MI-FTIR Spectrometry

As discussed in the previous sections of this review, MI-IR spectrometry has been used primarily for the characterization of unstable, reactive, and transient species and in studies of the stereochemical conformations of small molecules. To a lesser extent, MI-IR spectrometry has been used for the qualitative and quantitative analysis of stable compounds. However, few actual analytical applications have been reported. Wehry, Mamantov, and coworkers were the first to exploit the analytical capabilities of MI-FTIR; its use to analyze complex mixtures was a precursor to the recent combination of MI-FTIR spectrometry with gas chromatography.

Infrared spectrometry has been used to detect and identify eluents from a gas chromatograph for some time. In 1967, Low and Freeman [99] demonstrated the feasibility of using FTIR as a GC detection method. In conventional GC/FTIR spectrometry, the GC effluent is passed through a gold-coated light pipe, and spectra of the components

of interest are acquired "on-the-fly." Several excellent reviews of GC/FTIR applications have appeared in the literature.

Griffiths [100] presented an excellent discussion of the principles of FTIR spectrometry. Erickson [101] published a well-documented review of GC/FTIR, which covers the literature through 1978. Griffiths [102] discussed in detail the trade-offs that are necessary to optimize both GC and light-pipe FTIR performance, and Smith and Adams [103] discussed the compromises between optimum chromatography and IR spectrometry in GC/FTIR measurements.

An overview of the state of the art in hyphenated techniques was presented by Hirschfeld [104], who discussed the need for both efficient separation and high-resolution spectrometric detection in analytical applications; Hirschfeld suggested the potential of GC combined with MI-FTIR spectrometry. Herres [105] reviewed applications of GC/FTIR to the analysis of volatile species. Krishnan et al. [106] reviewed developments in GC/FTIR techniques through 1980, and Rossiter [107] briefly reviewed instrumentation developments in the same time period. Krishnan and Ferraro [108] in 1982 reviewed packed-column GC/FTIR. Wilkins [109] reviewed hyphenated techniques for the analysis of complex mixtures, Isenhour and Marshall [110] reviewed automated GC/FTIR and IR data processing, and Griffiths et al. [111] in 1983 reviewed developments in capillary column GC/FTIR but did not include coverage of GC/MI-FTIR techniques.

Krishnan [112] reviewed capillary column GC/FTIR applications through 1983, including the analysis of oils and perfumes, pesticides, and environmental pollutants, and pointed out that GC/MI-FTIR spectrometry might prove useful for these types of samples. Herres [113] briefly reviewed FTIR and presented examples of the state of the art in 1985. The requirements that must be met for picogram measurements were outlined by Hirschfeld [114].

Griffiths and Henry [115], in a review that appeared in 1986, provided an excellent overview of progress in GC/FTIR methods. They noted that the primary function of a GC/FTIR interface is identification, rather than quantification, which is usually better accomplished with a more sensitive and/or linear detector, such as the widely used GC flame-ionization detector (FID). The authors discussed in detail the characteristics of various GC/FTIR interface types, including light pipes and trapping interfaces with and without matrix isolation. In 1986, Griffiths and de Haseth [116] published an exhaustive and careful review of the field of FTIR spectrometry.

In 1987, Dixon and Eckers [117] reviewed current practice in capillary column GC/FTIR; and White [118] described developments in GC/FTIR instrumentation and software, discussed applications of

GC/FTIR to the analysis of complex mixtures, and included a brief treatment of GC/MI-FTIR spectrometry. Specific applications of a commercial instrument, the Cryolect system (Mattson Instruments, Madison, Wisconsin), that demonstrate the potential of GC/MI-FTIR are described in a collection of papers edited by Mattson and Carroll [119]. In addition to these general reviews, Wurrey and Gurka [120] recently reviewed environmental applications of GC/FTIR, including some work in GC/MI-FTIR.

GC/FTIR spectrometry is currently well-established as a powerful technique for identifying organic compounds in complex mixtures. Despite this success, applications of GC/FTIR methods have been limited by poor sensitivity; detection limits of on-the-fly GC/FTIR systems range from 5 to 50 ng for most compounds. Although these detection limits allow identification of the major components in complex mixtures, they are often inadequate for detecting the amounts of the minor components present in samples suitable for analysis by capillary GC methods. With the advent of GC/MI-FTIR spectrometry, mid-picogram detection limits have become achievable for polar analytes.

Conventional MI deposition techniques involve vaporizing the sample; therefore, MI-IR spectrometry should be amenable for the collection and subsequent spectral characterization of GC effluents. In 1979, Reedy and his colleagues [121] at the Argonne National Laboratory described a prototype GC/MI-FTIR system and outlined several conditions that must be met to obtain MI-FTIR spectra of components eluted from a GC column: (1) The technique must allow the collection of several components in rapid sequence. (2) The area over which the matrix is deposited must be minimized to optimize the IR absorption. (3) The rate of flow and condensation of the matrix-forming gas must be high enough to maintain proper dilution of the solute in the matrix.

The authors showed that MI conditions could be met with modest flow rates of matrix gas (less than 1 cm^3/min) for components having very narrow GC peaks (eluting in less than 10 s) provided that the total quantity of each component was relatively small (less than 10 nmol). However, the matrix gas flow rate is restricted to an upper limit of a few cubic centimeters per minute. This constraint is necessary because of the following three considerations. First, the heat of condensation of the matrix gas must not overheat the surface of the matrix. Second, the matrix gas must not be admitted more rapidly than it can be condensed; otherwise, the insulating value of the evacuated space surrounding the collector is diminished. Third, the flow rate must not become so high that the matrix becomes too thick, cracks, and detaches from the deposition surface.

The GC/MI-FTIR system developed at Argonne [121] consisted of a packed-column GC equipped with a flow-through thermal conductivity

detector, a cryogenic sample collector, a heated interface between the GC and cryogenic sample collector, and an FTIR spectrometer. During sample deposition, the GC effluent was mixed with a stream of argon matrix gas and then introduced into a molecular jet separator, where the helium carrier gas was removed. The components, separated by GC, were carried by the stream of argon into an evacuated, cryogenic sample collection apparatus.

The sample collector was a right-octagonal prism with mirror-finished faces. The design of this apparatus allowed a large number of separated components eluting from the GC to be collected, and it permitted the cryogenic surface on which the samples were deposited to be moved, which facilitated the collection and subsequent spectral examination of the eluents of interest. The device allowed the deposition of as many as 32 separate matrices. The MI-FTIR spectra of the matrix-isolated components were obtained by rotating the carousel until the component of interest was in the focus of the IR beam. Two concave mirrors were used to direct the IR beam to and from the deposition surface.

Preliminary tests of the GC/MI-FTIR system revealed the following: (1) The thermal contact across the movable interface between the sample collector and the cryostat was sufficient to promote condensation of the matrix gas. (2) The use of a heated transfer line to direct the matrix gas and sample onto the collector at a relatively high flow rate had no adverse effects on matrix deposition. (3) True matrix isolation conditions were achieved under the rapid condensation conditions. A mixture of three isomeric chlorophenols was separated on a packed GC column and deposited onto the cryogenic sample collector to illustrate the utility of the system. High-quality IR spectra were obtained for each isomeric compound. The sharpness of the OH stretching bands indicated that the phenols were collected under matrix isolation conditions.

In a parallel development, a group [122] at the University of Tennessee designed and constructed a GC/MI-FTIR interface which in principle was similar to the Argonne GC/MI-FTIR system [121]. In the Tennessee GC/MI-FTIR system, the effluent from an open-tubular, glass GC column was passed through a tee, where part of the effluent was directed to an FID and the remainder through a heated transfer line to a cryogenic sample collector. Nitrogen was used as both carrier and matrix gas. The collector was a 12-sided, gold-plated copper disk with 4- × 6-mm mirror-finished sampling surfaces. The sampling surfaces were positioned in turn by a stepper motor for deposition of the GC effluent and matrix and subsequent spectral acquisition. The optical interface used KRS-5 rods to direct the incident light toward the disk surface and to collect the reflected light from the surface. A diagram of this interface is shown in Fig. 2.

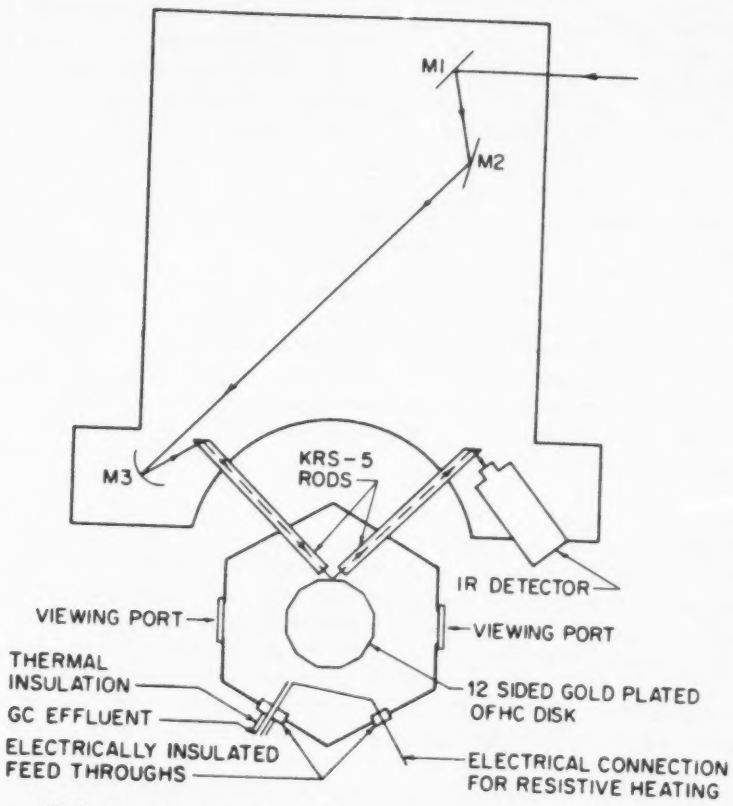


FIG. 2. Diagram of the GC/MI-FTIR optical interface developed at the University of Tennessee. M1 and M2 are planar mirrors; M3 is a spherical mirror. Reprinted from Ref. 122. Copyright 1981 by American Chemical Society.

To ensure that components from the GC effluents were matrix-isolated in the Tennessee system, Hembree et al. [122] compared MI-FTIR spectra of pure compounds collected from the GC effluent to spectra of the same compounds obtained by conventional Knudsen diffusion deposition [91]. For naphthalene and a wide variety of other PAHs, no differences in absorption maxima or bandwidths were observed. In a more rigid test, the MI-FTIR spectrum of phenol showed no signs of aggregation, evidencing true matrix isolation of the analyte.

The authors [122] noted that several improvements could be made to the Tennessee GC/MI-FTIR system. Use of a nondestructive GC detector would eliminate the need for the splitter arrangement and, if positioned upstream from the cryogenic collector, would facilitate the positioning of the deposition surface. Also, improvements in the optical efficiency of the system would permit more deposition surfaces on the cryogenic collector. Finally, the authors state that another form of MI spectrometry, such as molecular fluorescence, could also be used as a GC detection method. This topic is discussed in Section V-A of this review.

Bourne et al. [123] further evaluated the performance and the potential of the Argonne GC/MI-FTIR system. They concluded that GC/MI-FTIR spectrometry has the potential for identifying nanogram quantities of organic compounds eluted from capillary column GCs. The following two design considerations were among those discussed by these authors. First, the use of a capillary GC would eliminate the need for the molecular jet separator. This would increase the percentage of sample reaching the collector and would also allow the matrix gas to be added to, or used as, the carrier gas and passed directly to the collector. Second, the collector design in the original Argonne GC/MI-FTIR system [121] required each component from the GC effluent to be deposited in a discrete spot on the octagonal carousel. To expose a fresh cryogenic surface to the GC effluent stream, the carousel had to be rotated. A system was conceived that would use a continuously turning cylindrical collector instead of the octagonal carousel. This would allow the effluent of an entire GC run to be deposited on the cryogenic surface in a continuous matrix band.

The design and performance of a more advanced GC/MI-FTIR system were described in detail by Reedy and coworkers at the Argonne National Laboratory [124]. This system featured a cryogenic sample collector made from a gold-plated copper disk, 100 mm in diameter and 6 mm thick at the rim; the disk was polished to give a uniform mirror finish. A diagram of this interface is shown in Fig. 3. A splitter directed 10% of the GC effluent to an FID and the remaining effluent through a heated transfer line to the cryogenic disk. During a chromatographic run, the cryogenic disk was continuously rotated, and the separated components from the carrier gas stream were deposited in sequence in a track of an argon matrix on the rim of the cold mirror surface (see Fig. 4). The collimated beam from the FTIR system was focused by an off-axis parabolic mirror onto the cryogenic surface, collected by another off-axis parabolic mirror, and directed to a mercury-cadmium telluride (MCT) detector. The cryogenic disk was driven by a stepper motor and controlled through an indexer. The

computer-controlled stepper motor and indexer allowed the cryogenic disk to be positioned so that eluents having a selected retention time were in the focus of the IR beam. Thus, MI-FTIR spectra could be obtained of each sample component of interest. The system also included a Pyrex window as part of the vacuum chamber to allow observation of the deposition tip through a binocular microscope. This enabled the

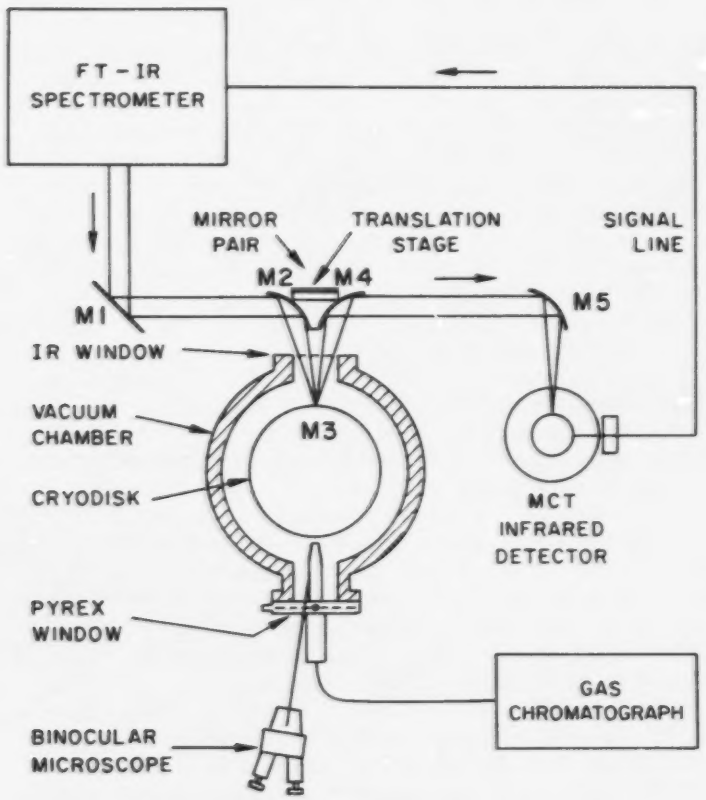


FIG. 3. Diagram of the GC/MI-FTIR optical interface developed at the Argonne National Laboratory. M1 is a planar mirror; M2, M4, and M5 are parabolic mirrors; and M3 is the mirrored surface of the cryogenic disk. Reprinted from Ref. 124. Copyright 1985 by American Chemical Society.

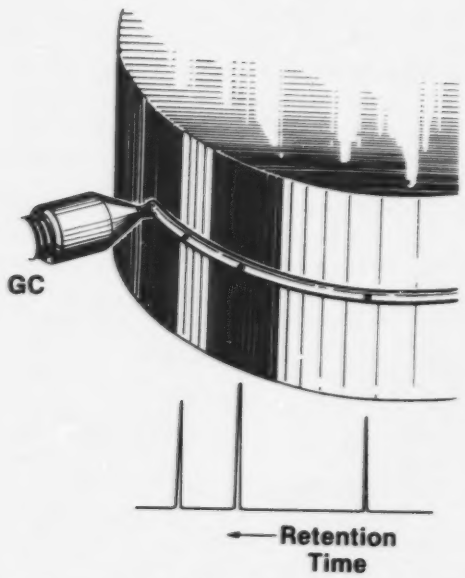


FIG. 4. Gas chromatographically separated compounds being deposited in a matrix of solid argon on a rotating cryogenic disk. The chromatogram in juxtaposition denotes the elution of chromatographically separated compounds. Reprinted from Ref. 124. Copyright 1985 by American Chemical Society.

position of the deposition tip with respect to the cryogenic collector surface to be monitored.

The authors [124] discussed the relationship between the quantity of sample, the diameter of the area over which the sample is deposited, and the observed IR absorbance. By taking into account the noise level of the FTIR spectrometer, they estimated the optimum S/N ratio for 1 ng of a strong IR absorber to be 30:1. The authors demonstrated the sensitivity of the system by identifying an MI-FTIR spectrum of 200 pg of isobutyl methacrylate.

The question of whether matrix isolation was achieved during rapid sample deposition was addressed by examining the MI-FTIR spectrum of acrylonitrile. The out-of-plane CH_2 vibrations of the vinyl group are a sensitive probe for matrix isolation conditions. If acrylonitrile is not sufficiently matrix-isolated, a cluster of IR peaks due to polymer formation is observed [84]. Comparison of an MI-FTIR spectrum of

acrylonitrile collected with the GC/MI-FTIR system with one obtained by conventional MI-FTIR techniques showed that true matrix isolation conditions were achieved under the rapid sample deposition conditions.

Related to the question of adequate matrix isolation is the question of proper carrier gas composition. The optimum matrix gas concentration is based on the quantity of material in each chromatographic peak, the width of the peak, and the carrier gas flow rate. Reedy et al. [124] showed that a high ratio of argon to helium in the carrier gas is not desirable because excessive dilution of the solute in the matrix reduces sensitivity. The optimum M/S ratio was found to be between 1000 and 100 to 1. A ratio lower than 100 to 1 produces a solid solution of solute in argon, in which case the solute is not truly matrix-isolated.

Reedy and associates [124] noted that to maintain chromatographic resolution on the cryogenic disk, two parameters must be controlled: the rate of rotation of the disk and the deposition tip position. The disk must rotate fast enough to avoid overlapping deposition of chromatographically resolved peaks. However, if the disk rotates too rapidly, the GC peaks are diffused over the cryogenic surface, and IR sensitivity is diminished. The optimum position of the deposition tip for maintaining chromatographic separation and IR sensitivity was determined empirically to be approximately one diameter of the transfer line tubing, in this case 150 μm.

These researchers illustrated the specificity of MI-FTIR spectra by discriminating between two closely related polychlorinated biphenyl (PCB) isomers. Also, two straight-chain hydrocarbons, which differed only in the number of CH_2 groups, were distinguished by their MI-FTIR spectra. The versatility of the GC/MI-FTIR system was illustrated by obtaining spectra of fluorene and pyrene. Analysis of these semivolatile compounds by the light-pipe GC/FTIR method is difficult because of the necessarily high operating temperature of the light-pipe interface, which limits sensitivity. However, in this type of GC/MI-FTIR system, IR sensitivity is independent of the operating temperatures of the injector, column, and transfer line.

Bourne et al. [125] discussed in detail the advantages of GC/MI-FTIR spectrometry over the more conventional light-pipe-based GC/FTIR systems. The principal advantage is an increase in sensitivity. The enhanced sensitivity of GC/MI-FTIR is achieved in five specific areas: (1) The amount of light passing through the analyte is limited only by the saturation point of the IR detector. In contrast, on-the-fly systems must strike a compromise between IR signal intensity and cell volume of the light pipe. As the cell volume is decreased to maintain chromatographic resolution, the signal intensity is diminished. (2) The analyte is concentrated in a small cross-sectional area on the

cryogenic surface. Because IR sensitivity is directly proportional to concentration per unit volume, sensitivity is enhanced. (3) Most of each GC peak is held in the IR beam during each scan, whereas it is difficult to introduce the entire GC peak into a light pipe at one time. (4) Because the sample is frozen on the collector indefinitely, unlimited signal-averaging is allowed on any GC peak. Light-pipe systems are limited to scan times no longer than the GC peak width, which is typically 2-5 s; thus, only a few interferograms can be collected per GC peak. (5) Spectral bands are narrower for matrix-isolated compounds than for compounds in the vapor or condensed phase because band broadening due to molecular rotation and intermolecular interactions is eliminated under MI conditions. As a result, absorbance values of the band maxima for matrix-isolated compounds are greater than for those measured in the vapor phase.

The GC/MI-FTIR systems also have other advantages. With GC/MI-FTIR spectrometry the separation and detection of individual components in a complex mixture are independent steps. Therefore, the chromatography and spectrometry can be optimized without compromising one or the other. For instance, the enhanced sensitivity of GC/MI-FTIR allows high-resolution, narrow-bore, thin-film capillary columns to be used. In addition, the flow rate and GC peak width do not need to be adjusted to match the interface. Also, light-pipe-based GC/FTIR is of limited use for analyzing compounds with high boiling points because of the inverse relationship between IR signal intensity and operating temperature of the interface. As shown previously [124], this is not a problem with GC/MI-FTIR. Postrun IR data acquisition, which is characteristic of the GC/MI-FTIR experiment, also has several advantages over real-time GC/IR scanning. Spectra are obtained for only those GC peaks of interest, as opposed to continuous data acquisition with a light-pipe system. This feature of GC/MI-FTIR spectrometry optimizes computer storage space and frees the system for data processing of earlier runs and routine FTIR measurements while the GC effluents are being deposited.

Schneider et al. [126, 127] assayed the performance characteristics of the Argonne GC/MI-FTIR system [124] in comparison to a commercial light-pipe-based GC/FTIR system. In general, detection limits for most compounds were less than 1 ng with the GC/MI-FTIR system, which is comparable to detection limits characteristic of scanning GC/MS. The limit of detection for the light-pipe-based system depended on the volatility of the sample: 20-200 ng for compounds of high volatility and 200-2000 ng for compounds of low volatility. The sharp features characteristic of MI-FTIR spectra allowed for greater molecular specificity with GC/MI-FTIR than did the vapor-phase spectra obtained with the light-

pipe-based GC/FTIR system. This enhanced specificity aids in identification of components in complex mixtures and facilitates differentiation between isomers. Disadvantages of the GC/MI-FTIR system included a high initial cost and, because it is a two-step process as opposed to on-the-fly spectral acquisition, an increase in the time required for each analysis. The authors concluded that, if a sufficient amount of sample is available for analysis, the light-pipe interface is preferable for functional group surveys and for the rapid characterization of mixtures when cost, time, and operator experience are a consideration. The GC/MI-FTIR interface is indicated for trace analysis, especially when molecular specificity is essential.

The commercial availability of a GC/MI-FTIR instrument, the Cryolect system (Mattson Instruments, Inc., Madison, Wisconsin), which is based on the prototype developed at the Argonne National Laboratory, was announced in 1984 [128].

3. GC/MI-FTIR Spectra of Stable Organic Compounds

Infrared spectrometry is a powerful tool for the elucidation of molecular structure. The positions and intensities of IR absorption bands are very sensitive to changes in molecular structure and geometry. However, the appearance of an IR spectrum for a given compound also depends on the phase in which the sample was prepared. The most obvious difference is the enhanced spectral definition that is observed for spectra measured under matrix isolation conditions as compared to spectra measured for samples in the condensed phase. Other more subtle differences, such as shifts in band intensity, changes in relative band intensity, and changes in the actual number of absorption bands, can also occur when IR spectra are measured under MI conditions. If GC/MI-FTIR spectrometry is to become a useful analytical tool for the identification of unknown components in complex mixtures, matrix effects on the appearance of IR spectra must be well-characterized.

In a recent series of articles, Coleman and Gordon [129-138] reported the examination of the MI spectra of organic compounds. They compared MI spectra, which were measured on a commercial GC/MI-FTIR system, to vapor-phase (VP) and solid-state/solution (SS) spectra of several classes of compounds, including amides, lactones, lactams, esters, carboxylic acids, alcohols, phenols, ketones, aldehydes, halogenated esters, β-diketones, alkenes, catechols, resorcinols, hydroquinones, and diols. These articles focused on trends in functional group absorption frequencies, factors that influence the extent of matrix isolation, and spectral features that are unique to MI spectra. Particular attention was given to the splitting of the carbonyl group absorption band in selected compounds.

In general, Coleman and Gordon found that the absorption maxima for functional group frequencies, such as carbonyl-group or hydroxy-group stretching frequencies, obtained under MI conditions were intermediate to those found in the literature for VP (higher energy) and SS (lower energy) spectra. In studies of specific classes of compounds, Coleman and Gordon found that the carbonyl-group frequencies of a series of aliphatic carboxylic acids measured under MI conditions more closely resembled the VP values than the SS values [129]. Also, the energies of the OH group stretching frequencies for selected carboxylic acids, alcohols, and phenols were up to 400 cm^{-1} higher for the MI and VP spectra than for the SS spectra. These two observations were attributed to the absence of intermolecular hydrogen bonding under MI and VP conditions. The SS spectra of sterically hindered, alkyl-substituted phenols also exhibited shifts in the OH stretching frequency to higher energy. Apparently, the bulk of the alkyl group interrupts the OH—OH intermolecular bonding interactions in the SS case. Under MI and VP conditions, the molecules are sufficiently isolated and no intermolecular interactions occur. As mentioned earlier [121], the absence of intermolecular interactions in phenols is a test for true matrix isolation.

For the most part, trends as a function of structure and substituent group effects that were established in VP spectra existed under MI conditions. Ring strain increased the carbonyl stretching frequency for cyclic ketones, esters (lactones), and amides (lactams) [129]. The OH stretching frequency systematically shifted to lower energy for primary, secondary, and tertiary alcohols in both MI and VP conditions, where no intermolecular hydrogen bonding occurs [129]. Shifts in the carbonyl frequencies to lower energy were observed in all three phases (MI, VP, and SS) when methyl substitutions were made on the carbon(s) alpha to the carbonyl group in a series of linear ketones [130]. A shift in the carbonyl frequency to lower energy was also observed when the carbonyl group was positioned toward the center of a long-chain hydrocarbon. Unsaturation, in the form of a double bond or an aromatic ring, shifted the carbonyl band to lower energy. Substitution of different alkyl groups on the ester linkage in a series of normal esters also shifted the carbonyl band [130].

For aldehydes, when an alkyl group was replaced by a phenyl group, the carbonyl band shifted to lower energy [132]. Also, substitution ortho to the carbonyl on an aromatic ring shifted the carbonyl band maximum to lower energy. If a polar group was substituted in the ortho position, this shift was more dramatic (approximately 40 cm^{-1}).

For saturated lactones, the carbonyl absorption approached energies associated with open-chain esters as the ring size increased [135]. Lactones in which the carbonyl group can participate in conjugation exhibited carbonyl absorption bands at lower energies than the unconjugated analogs. Lactams also exhibited an increase in carbonyl stretching frequency with a decrease in ring size [135]. Substitution on the nitrogen of the lactam resulted in a decrease in the energy of the carbonyl absorption band.

Coleman and Gordon [137] also used GC/MI-FTIR to investigate keto-enol tautomerization in selected β-diketones. Keto-enol tautomerization is a function of temperature. Therefore, significant differences might be expected between the MI spectra obtained at 10 K and the VP spectra obtained at 500 K. However, under typical experimental conditions for GC/MI-FTIR spectrometry, the analyte passes through a heated (473-523 K) transfer line before it is deposited on the cryogenic disk. As discussed in Section III-C of this review, the assumption that most conformers trapped in low-temperature matrices are in the proportion corresponding to the equilibrium that existed in the gas phase is generally borne out [48]; exceptions can be expected for conformational equilibria with comparatively small barriers to internal rotation (less than about 6 kJ/mol). Similar behavior should be expected for tautomeric species. Coleman and Gordon [137] showed that the equilibrium between the keto and enol tautomers that exists for selected β-diketones in the VP state also exists under GC/MI-FTIR conditions. This result is not surprising, because the potential barriers for this interconversion are relatively large; for example, the vapor phase barrier for acetylacetone is about 8 kJ/mol [139].

The MI-FTIR spectra for a series of straight-chain and branched alkenes exhibited much sharper features than did the VP or SS spectra [137]. However, the $=C-H$ stretching frequency was essentially the same (± 5 cm^{-1}) for all three phases. The similarity of the MI, VP, and SS spectra indicates that the less polar alkenes have fewer intermolecular interactions than the more polar compounds, such as aldehydes and ketones.

Coleman and Gordon [138] examined the effect of molecular geometry on the degree of intramolecular and intermolecular hydrogen bonding in a series of catechols, resorcinols, other diols, and hydroquinones. Vapor-phase and matrix-isolated spectra of catechol (1,2-dihydroxybenzene) were very similar; both exhibited two OH stretching frequencies, which were assigned to the intramolecular hydrogen bonding conformation and the nonhydrogen bonding conformation. Substitution of a bulky alkyl group in the 3-position on the aromatic ring of catechol shifted the OH stretching frequency assigned to the intramolecular

conformation to lower energy. When an aldehyde group was inserted in the 3-position on the ring, only one OH absorption band was observed. This indicated that the molecule was predominantly in the intramolecular hydrogen bonding conformation. The authors also observed a broad absorption band centered at approximately 3430 cm^{-1} in the MI-FTIR spectra of the catechols at levels of less than 20 ng on the cryogenic disk. This indicated extensive intermolecular hydrogen bonding, a form of nearest-neighbor interactions or aggregations. These interactions were more evident in the MI-FTIR spectra of catechols with bulky substituents. The MI-FTIR spectrum of resorcinol (1,3-dihydroxybenzene) indicated extensive nearest-neighbor interactions at the 10-ng level. However, the MI-FTIR spectrum of 4,6-dichlororesorcinol contained only one sharp absorption in the OH stretching region. The intramolecular interactions between the OH and Cl groups apparently are so strong in 4,6-dichlororesorcinol that no indications of intermolecular interactions are evident in the MI-FTIR spectra, even at the 50-ng level. The MI-FTIR spectra of the hydroquinones exhibited most of the characteristics displayed by the catechols and resorcinols.

The MI-FTIR spectra of several compounds in a series of diols exhibited OH stretching frequencies due to intramolecular and intermolecular hydrogen-bonding, as well as those from the free OH group [138]. In many cases the VP spectra did not reveal any intramolecular interaction. Neither VP nor MI evidenced intramolecular interactions when the size of the ring that could be formed by intramolecular hydrogen bonding exceeded six. In these larger diols, the OH stretching region was dominated by broad absorptions typical of intermolecular hydrogen bonds. Again, this indicated extensive interactions between molecules at levels of solute previously thought to be adequate for matrix isolation.

Coleman and Gordon [130] observed that the carbonyl absorption band for selected aliphatic ketones was split on the order of 5 to 10 cm^{-1} when bulky substituents were located in the alpha position [130]. An example of this splitting can be observed in the MI-FTIR spectrum of 3,3-dimethyl-2-butanone (see Fig. 5). This splitting was not observed in unbranched ketones. Further investigation of a series of esters and ketones revealed that molecular aggregation, which would be revealed by varying the M/S ratio, was not the predominant cause of the band splitting [131]. Steric bulk of the alkyl substituents was also ruled out as the cause of the splitting phenomenon, although the splitting was more pronounced in sterically hindered esters and ketones. The authors postulated that the splitting might be due either to the presence of molecules in different conformations or in different matrix sites, or to other effects associated with molecule-matrix interactions. Also, the ratio of the two distinct carbonyl absorption bands in methyl acetate was not

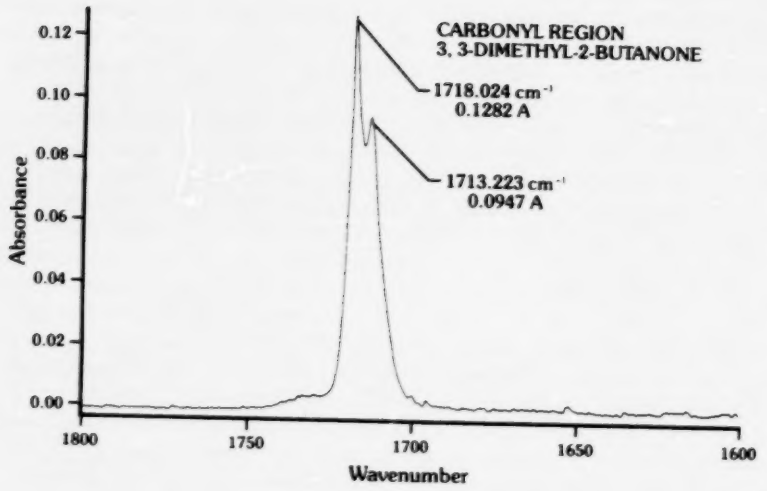


FIG. 5. MI-FTIR spectrum of 3,3-dimethyl-2-butanone showing split absorption in the carbonyl region. Reprinted from Ref. 130. Copyright 1987 by Society for Applied Spectroscopy.

constant over the range of 1.25 to 50 ng of solute deposited on the cryogenic disk. This indicated the presence of two individual carbonyl-containing species whose molar ratio changed as a function of the M/S ratio.

To investigate further the factors that affect the splitting of the carbonyl band, Coleman and Gordon [132] examined the MI-FTIR spectra of a series of aldehydes and carboxylic acids. Low-boiling and nonlinear aldehydes with fewer than five carbon atoms exhibited split, well-resolved carbonyl absorptions with a full width at half-height (FWHH) of approximately 2 cm^{-1}; whereas the higher boiling aldehydes with six or more carbon atoms exhibited single, but broadened, absorption bands (FWHH of 10-12 cm^{-1}). These results indicated that the two types of aldehydes were not matrix-isolated to the same extent. Because the amount of solute was the same in all cases, the geometry of the solute apparently influences the extent of matrix isolation. Coleman and Gordon offered two possible explanations to account for the splitting in the low-boiling/nonlinear aldehydes: (1) monomer-polymer isolation or nearest-neighbor interactions and (2) conformer isolation. The small

FWHH values of 2 cm^{-1} indicate minimal nearest-neighbor effects and suggest that conformer isolation was the cause of the band splitting. Ample precedent for conformer isolation under MI conditions has been reported, as discussed in Section III-C of this review. The MI-FTIR spectra of the series of carboxylic acids as a function of the M/S ratio also revealed a stereochemical effect; in general, the carbonyl band for the series of carboxylic acids broadened as the chain length increased.

A systematic investigation of the splitting of the carbonyl absorption band in selected organic compounds was carried out by Coleman and Gordon [133]. By varying the M/S ratio and the type of matrix gas (either argon or xenon), the observed splitting could be attributed to both conformer isolation and aggregation in the matrix. In general, band splitting was observed in linear and branched compounds containing less than five carbons. Compounds having more than five carbons displayed only band broadening.

To test for aggregation, Coleman and Gordon adjusted the chromatographic conditions to cause abnormal GC peak broadening [133]. This, in effect, varied the M/S ratio over three orders of magnitude and produced a gradient in the quantity of solute deposited in the matrix, ranging from 0.250 ng at the leading and trailing edges of the GC peak to 400 ng at the GC peak maximum. Examination of the MI-FTIR spectra of methyl acetate under these conditions revealed that the FWHH increased, and a new absorption band of lower energy (which eventually had the larger absorbance value) appeared as spectra were taken along the ascending slope of the GC peak. Spectra obtained on the descending portion of the GC peak retraced the trend to a single absorption band. This type of behavior indicates aggregate formation within the matrix. Changing the argon concentration in the matrix gas confirmed that the M/S ratio significantly influences the profile of the carbonyl absorption.

These authors found that aggregation was not, however, the universal cause for the splitting of the carbonyl band in all compounds. The MI-FTIR spectrum of phenyl acetate contained multiple (four) carbonyl absorption bands. Examination of the MI-FTIR spectra of this compound under broadened chromatographic conditions, adjusted as before, revealed the presence of conformers (M/S-independent) and an aggregate (M/S-dependent). However, for trimethylacetaldehyde, no aggregation was indicated, and the split absorption was attributed to conformer isolation.

To help characterize the effect of matrix conditions on spectral appearance, the matrix gas, for example, argon or xenon, can be varied. Because xenon has a larger atomic diameter than argon, the characteristics of the respective matrices, such as the nature of the

trapping sites and the extent of nearest-neighbor interactions, are not likely to be similar. Examination of the MI-FTIR spectrum of methyl acetate using xenon instead of argon as the matrix gas revealed the following: the FWHH was much narrower, the ratio of the split absorption bands changed, the carbonyl band maxima were at lower energy, and the band maxima were better resolved. These results indicate that aggregate formation and nearest-neighbor interactions are reduced when xenon is used as the matrix gas. This is consistent with the larger atomic diameter of xenon. In contrast, the IR spectrum of trimethylacetaldehyde in a xenon matrix was not different from that in argon, which indicated that trimethylacetaldehyde was present in the matrix as conformers rather than aggregates.

Coleman and Gordon [133] presented general guidelines for the interpretation of the carbonyl group absorption band in MI-FTIR spectra. When multiple bands are observed, aggregation and/or conformer isolation could be present; thus, an M/S study to test for absorbance ratio changes is indicated. If absorbance ratios vary, the M/S ratio must be increased by decreasing the amount of solute or by increasing the amount of matrix gas until no further change is noted.

Coleman and Gordon [134] also found that the low-temperature conditions of the GC/MI-FTIR experiment allowed the observation of discrete rotational isomers not seen before in VP spectra of a series of halogenated esters. Several alkyl- and allyl-substituted chloroacetates exhibited split carbonyl absorption bands that could not be attributed to aggregation. For compounds with no possible rotational isomers, only one absorption band was observed. Steric bulk on the carbon of the ester linkage was shown to increase the complexity of the carbonyl absorption.

In a reexamination of the MI-FTIR spectra of a series of lactones and lactams, Coleman and Gordon [135] concluded that the split carbonyl absorption observed in these compounds was not attributable to aggregation and was most likely due to isolation of discrete conformers in the matrix. This, however, did not account for all of the observed splittings. Additional ring strain caused by unsaturation was found to significantly reduce the complexity of the carbonyl absorption bands. The insertion of a double bond hinders the flexibility of the five-membered ring, which reduces the conformational possibilities. This resulted in a less complex carbonyl absorption region. The same effect was observed when an aromatic ring is fused to a five- or six-membered ring. However, if delocalization of electron density is possible, as in phthalide and coumarin, by conjugation of the aromatic ring and carbonyl group, the carbonyl group absorption remained complex.

Coleman and Gordon [136] also examined the effect of ring strain on the carbonyl absorption bands for a series of ketones. The carbonyl band became more complex with increasing ring size (increased flexibility of the ring) for a homologous series of cyclic ketones. The FWHH also increased with ring size. As with the lactams and lactones, unsaturation alpha to the carbonyl group simplified the carbonyl absorption. This effect was shown to have a diminishing influence on the carbonyl absorption as the ring size increased. Fusion of an aromatic ring to the cyclic ketones also simplified the MI-FTIR spectra, but not as dramatically as for the lactams and lactones. Bicyclic ring systems exhibited very simple carbonyl absorptions, which was attributed to an increase in rigidity and ring strain. Again, if unsaturation was alpha to the carbonyl group, the carbonyl absorptions were simplified. In addition, rotational isomers of halogen-substituted ketones were isolated in the argon matrix.

In related work, Rogers and White [140] evaluated the use of computer-assisted searches of an IR spectral library of vapor-phase compounds for the characterization of MI spectra generated by GC/MI-FTIR analyses. The authors obtained MI-FTIR spectra of 40 compounds known to be in the EPA vapor-phase IR library. The MI-FTIR spectra were collected at resolutions ranging from 1 to 4 cm^{-1}, then "de-resolved" to 16 cm^{-1} by using a Fourier-domain deconvolution routine. A square-difference search algorithm was used to search the EPA vapor-phase IR library for the best match of the smoothed MI-FTIR spectra.

The success of the library searching procedure depended on the extent of band broadening caused by spectral smoothing. Optimum smoothing and search parameters varied considerably for individual MI-FTIR spectra and were structure-dependent. If the band-broadening factor was optimized for each spectrum, 92.5% of the MI-FTIR spectra were identified as one of the top five search matches. However, only 70% of the MI-FTIR spectra were identified when uniform band-broadening parameters were used.

4. Analytical Applications of GC/MI-FTIR Spectrometry

Most published analytical applications of GC/MI-FTIR spectrometry have involved the analysis of environmentally important compounds. One particular class of compounds that has received much attention is the polychlorinated dibenzo-p-dioxins (PCDDs). The presence of PCDDs in the environment poses a significant risk to animal, and possibly human, health. Considerable effort and expense have gone into decontaminating affected sites throughout the world. Unfortunately, the analysis of PCDD-contaminated samples can be a very difficult task.

This difficulty is due in part to the existence of 76 PCDD isomers, which include 22 isomers in the most widely studied subset, the tetrachlorodibenzo-p-dioxins (TCDDs). Because toxicity is related to molecular structure, methods are needed to unambiguously distinguish the PCDD isomers. The need for isomer specificity is exemplified by the millionfold difference in animal toxicities between 1,2,3,4-TCDD and the most toxic PCDD isomer, 2,3,7,8-TCDD. Current PCDD analyses are most often accomplished by correlating GC/MS results with GC retention times of pure reference standards. These methods, although very sensitive, are not isomer-specific and are hindered by the presence of coeluting isomers and the limited availability of pure reference standards. In 1987, Grainger and Gelbaum [141] published the vapor-phase IR spectra of the 22 TCDD isomers. Gurka and coworkers [142] previously published diffuse reflectance infrared Fourier transform (DRIFT) spectra of the same set of compounds. Both reports [141, 142] demonstrate that the individual TCDDs have unique IR characteristics. Several recent publications [143-148] have illustrated the applicability of GC/MI-FTIR to the analysis of PCDDs.

Reedy et al. [124] published the first MI-FTIR spectrum of 2,3,7,8-TCDD in 1985 to demonstrate the use of GC/MI-FTIR for PCDD analysis. In 1986, Wurrey et al. [143] showed that the sensitivity of GC/MI-FTIR for TCDDs is in the picogram range and that GC/MI-FTIR results were comparable to those obtained by GC/MS for the determination of 2,3,7,8-TCDD in an environmental sample. The same research group [144] also published MI-FTIR spectra of 2,3,7,8-TCDD and ^{13}C-2,3,7,8-TCDD. The IR peaks in the MI-FTIR spectrum of the labeled compound were sufficiently shifted in frequency from those of the native 2,3,7,8-TCDD to allow a mixture of the two isotopomers to be resolved. Thus, the commonly used GC/MS method for determining 2,3,7,8-TCDD by adding ^{13}C-2,3,7,8-TCDD to the sample as an internal standard would also be applicable to GC/MI-FTIR spectrometry. In fact, this capability allows the analysis of the same sample extract by both GC/MS and GC/MI-FTIR. In a later report, however, Holloway et al. [145] showed that the spectrum previously [144] assigned to ^{13}C-2,3,7,8-TCDD was actually ^{13}C-2,3,7-trichlorodibenzo-p-dioxin. The correct spectrum of ^{13}C-2,3,7,8-TCDD was published [145] and indeed exhibited vibrational frequencies significantly different from those of the native 2,3,7,8-TCDD. These results validated the conclusion of Wurrey et al. [144] that the isotopic dilution method for quantifying TCDD is applicable to GC/MI-FTIR.

Gurka et al. [146] collected and compared the micro-DRIFT spectra and the MI-FTIR spectra of the 22 TCDD isomers. Although the general spectral features of the DRIFT and the MI-FTIR spectra of

2,3,7,8-TCDD were similar, differences in the IR frequencies for specific bands ranged from less than 1 cm^{-1} to greater than 119 cm^{-1}. However, in general, the most intense band(s) in the respective MI-FTIR spectra of the 22 TCDD isomers were within approximately ± 4 cm^{-1} of the most intense band(s) in the DRIFT spectra. Two soil extracts, shown previously by GC/MS to contain 40-ppm and 500-ppb levels of 2,3,7,8-TCDD, respectively, were analyzed by GC/MI-FTIR spectrometry. Identifiable spectra of 2,3,7,8-TCDD were obtained from both samples either directly or through spectral subtraction.

Brasch [147] used GC/MI-FTIR to identify six specific TCDD isomers in a complex environmental sample. Also, one unresolved GC peak was shown to contain ^{13}C-2,3,7,8-TCDD, 2,3,7,8-TCDD, 1,2,3,8-TCDD, and 3,4,6,7-tetrachlorodibenzofuran (TCDF). The author noted that GC/MS could not discriminate between the 1,2,3,8- and the 2,3,7,8-TCDD isomers. A second unresolved peak was shown to contain ^{13}C- and ^{12}C-2,3,7,8-TCDF, as well as other unidentified TCDF isomers. The ability to distinguish between the native compounds and the ^{13}C-labeled internal standards again supports the potential of GC/MI-FTIR for the quantitative analysis of PCDDs.

The research reported by Holloway et al. [145] included a composite intensity-frequency chart derived from MI-FTIR spectra of the 22 TCDD isomers. The chart illustrates that each TCDD isomer has a unique MI-FTIR spectrum. Spectra of 1,2,3,4-TCDD at levels of 20, 2.5, 0.30, and 0.156 ng were recorded. The spectrum acquired for 0.156 ng was still clearly identifiable as 1,2,3,4-TCDD but required the coaddition of 5000 scans. In these experiments, Beer's law was obeyed over the 0.156- to 20-ng range, and the relative standard deviations for three replicate injections varied from 4.6% (20 ng) to 23% (0.156 ng).

The difficulty in obtaining pure, well-characterized reference standards of the TCDD isomers has led to several discrepancies in the literature concerning isomer assignments. Grainger et al. [148] attempted to resolve some of these discrepancies by obtaining MI-FTIR spectra of the 1,2,4,7- and 1,2,4,8-TCDD isomers that had been previously separated by reversed-phase high performance liquid chromatography (HPLC). They made isomer assignments in terms of a qualitative, valence-bond approach and empirically derived estimates of asymmetric stretching frequencies for the TCDD ether linkage. Despite the structural similarities between the 1,2,4,7- and the 1,2,4,8-TCDD isomer pair, three regions of the MI-FTIR spectra (1600-1400, 1300-1280, and 1000-800 cm^{-1}) exhibited sufficient differences to enable isomer differentiation (see Fig. 6). In general, the estimated ether-linkage asymmetric stretching frequencies for the 22 TCDD isomers

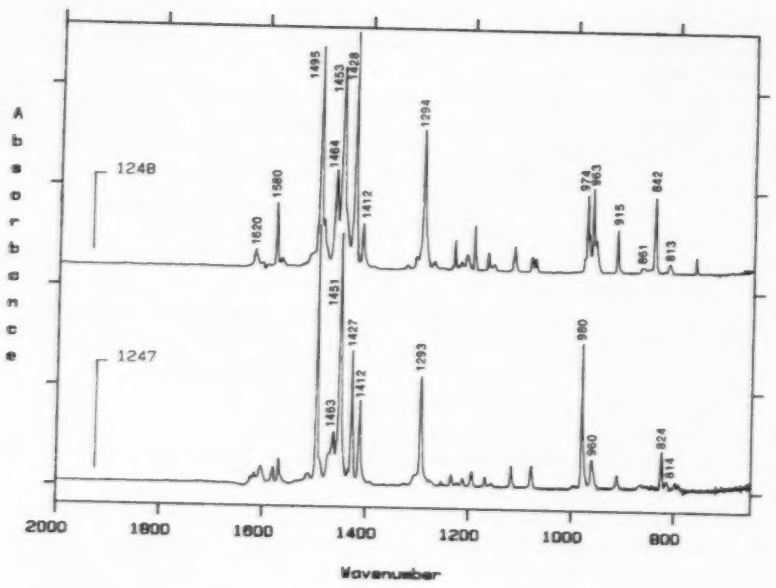


FIG. 6. MI-FTIR spectra of HPLC-separated 1,2,4,7- and 1,2,4,8-tetrachlorodibenzo-p-dioxin isomers. Reprinted from Ref. 148. Copyright 1988 by Society for Applied Spectroscopy.

showed an excellent correlation with the observed stretching frequencies. However, ambiguities in the specific assignments of the 1,2,4,7- and the 1,2,4,8-TCDD isomer pair remained, and the authors concluded that definitive isomer assignment must ultimately be determined by X-ray crystallography. Proton nuclear magnetic resonance should prove useful in this determination.

Another class of compounds that poses a significant risk to the environment is the polychlorinated biphenyls. The identification of PCBs by current GC methods with electron capture detection is based on recognition of characteristic patterns in the sample chromatogram that can be compared to reference chromatograms of commercially produced mixtures. If a distinct pattern is not found, or if many impurities are present, the analysis can be complex and time-consuming. Schneider et al. [149] used GC/MI-FTIR to identify the components

responsible for more than 98% of the total integrated GC peak area in a commercially produced PCB mixture. Specific PCBs were identified by comparing MI-FTIR spectra of the GC components to reference MI-FTIR spectra of individual PCB standards. Some components of the chromatogram could not be identified because the authors' reference MI-FTIR spectral library contained spectra of only 40 PCB standards out of the possible 209 congeners. Detection limits for PCBs were estimated to be in the 1- to 10-ng range on the basis of a 10 to 1 S/N ratio needed for identification, which was specified by the authors.

In work at the U.S. Environmental Protection Agency [150-152], the potential of GC/MI-FTIR for characterizing semivolatile organic compounds (compounds with vapor pressures between roughly 10^{-2} and 10^{-8} kPa at ambient temperatures) in environmental air sample extracts has been evaluated. In particular, the ability of GC/MI-FTIR to identify PAHs in complex environmental samples and to discriminate between isomeric PAHs has been demonstrated.

In a preliminary study by Childers et al. [150], an extract of the National Bureau of Standards (NBS) standard reference material 1649 (urban dust/organics) was analyzed by GC/MI-FTIR spectrometry. A component of the extract that had previously been identified as anthracene by supercritical fluid chromatography was unambiguously identified as phenanthrene by GC/MI-FTIR. Fluoranthene, pyrene, benzo[b]fluoranthene, chrysene, triphenylene, benzo[e]pyrene, and benzo[ghi]perylene were also identified in the extract. Specific PAHs were identified in unresolved GC peaks by using spectral subtraction followed by computer-assisted library searches.

Wilson et al. [151] used GC/MI-FTIR to identify specific PAHs in extracts of particulate matter from diesel-powered automobiles, urban air samples, and wood-burning stove emissions. The authors identified several target PAHs and distinguished between isomeric PAHs that cannot be distinguished by GC/MS or other commonly used analytical techniques. The isomers chrysene and triphenylene, which coeluted under the chromatographic conditions used in this study, were both identified in the extract from diesel exhaust. The potent mutagen 1-nitropyrene was also identified in the diesel exhaust emissions extract. A broad, unresolved GC peak in the chromatogram of the urban air particulate matter extract was shown to contain the three benzofluoranthene isomers, each of which has a unique MI-FTIR spectrum (see Fig. 7). Oxygenated PAHs, such as 9-fluorenone and anthraquinone, were identified in the wood-burning stove emission extract.

Childers et al. [152] examined an extract of particulate emissions from a wood-burning stove. Several specific PAHs, including 9-fluorenone, anthraquinone, phenanthrene, fluoranthene, pyrene, benz[a]-

anthracene, chrysene, triphenylene, benzo[e]pyrene, and benzo[a]-pyrene, were identified in the extract. High levels of retene (1-methyl-7-isopropylphenanthrene), which is a compound that has been proposed as a woodsmoke marker compound for source apportionment, were found in this sample (see Fig. 8). A preliminary investigation of the potential of GC/MI-FTIR for the quantitative analysis of PAHs, using 1-methylbenz[a]anthracene as an internal standard, showed a relative standard deviation of 15% for IR absorbances in replicate analyses of standard PAH solutions.

Hembree et al. [122] analyzed extracts of solvent-refined coal and coal-derived crude oil on the Tennessee GC/MI-FTIR system. The chromatogram of the aromatic fraction of coal-derived crude oil was very complex. As a result, discrete regions of the chromatogram were

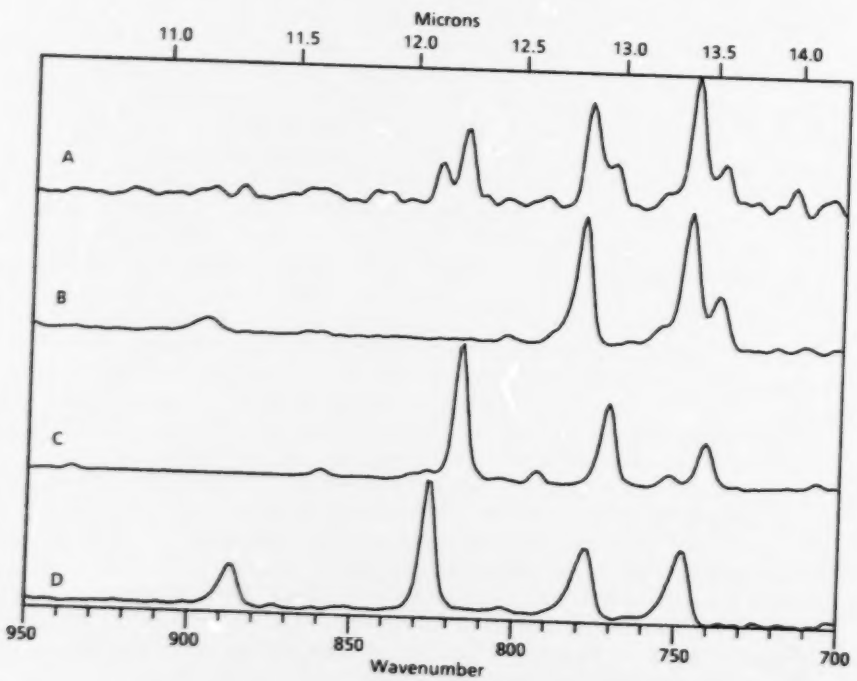


FIG. 7. MI-FTIR spectra of (A) component of an extract of urban air particulate matter, and reference MI-FTIR spectra of (B) benzo[b]-fluoranthene, (C) benzo[j]fluoranthene, and (D) benzo[k]fluoranthene.

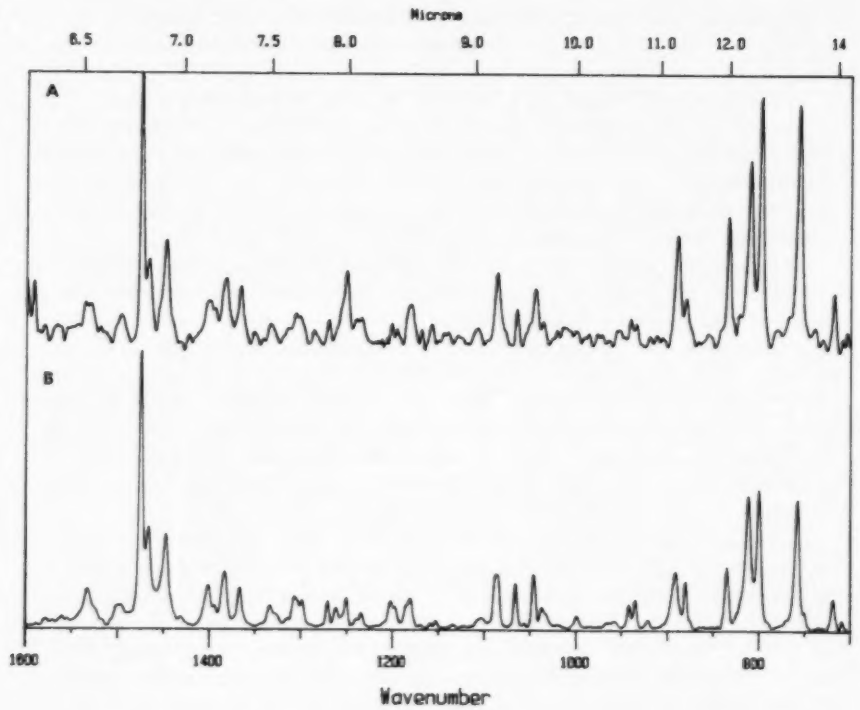


FIG. 8. MI-FTIR spectra of (A) component of an extract of particulate emissions from a wood-burning stove and (B) reference MI-FTIR spectrum of retene, 1-methyl-7-isopropylphenanthrene.

deposited on four separate disk surfaces. The major components of the four regions of the chromatogram were determined to be naphthalene (region 1); 1,4-dimethylnaphthalene, indole, 2-methylindole, and 3-methylindole (region 2); phenanthrene and carbazole (region 3); and pyrene (region 4). The quantitative capabilities of the system were illustrated by determining the phenanthrene content of the solvent-refined coal extract. Three quantitative methods were compared: (1) GC/FID peak height measurement using standard addition; (2) GC/MI-FTIR peak height using standard addition; and (3) GC/MI-FTIR peak height using a calibration curve for pure phenanthrene obtained in separate experiments. Results of all three methods were in close agreement (± 0.02 mg/g). In another experiment, quantitative analysis of

NBS standard shale oil by GC/MI-FTIR for phenol, o-cresol, and 2,4,6-trimethylpyridine yielded results comparable to those obtained by LC, GC, and GC/MS.

Robinson and Vizcaino [153] used GC/MI-FTIR to confirm the presence of benzo[a]pyrene metabolites in rat tissues. Laboratory rats were injected with sesame oil containing benzo[a]pyrene and then sacrificed. Analysis of acetone extracts of the rat tissue by GC/MI-FTIR confirmed the presence of 7-methylbenzo[a]pyrene and 6-methylbenzo-[a]pyrene, which could not be separated chromatographically.

In another application of GC/MI-FTIR to environmental analyses, Holloway et al. [145] studied the composition of the pesticides Fonofos and Terbufos to develop the methodology needed to investigate their persistence in the environment and to differentiate between the two compounds in groundwater samples. The two related pesticides exhibited similar but significantly different MI-FTIR spectra. Reproducibilities of absorptivities of the major IR peak in Fonofos were comparable to those of the relative weight response determined by GC/FID. The study showed that Fonofos decomposed at a much lower rate than Terbufos under simulated environmental conditions.

Mossoba and coworkers at the U.S. Food and Drug Administration [154] used GC/MI-FTIR to identify and quantify ethyl carbamate (urethane) at the part-per-billion level in alcoholic beverages and foods. Ethyl carbamate is a known animal carcinogen and is a natural product of many fermentation processes. Existing methods for monitoring ethyl carbamate at the levels of interest are often limited by interferences. In this study, extracts from whiskey, bread, yogurt, beer, soy sauce, and blue cheese were analyzed.

Identifiable spectra of ethyl carbamate, which were obtained with only moderate signal averaging (300 scans), were reported for levels as low as 0.6 ng. For the quantitative analyses, calibration curves for ethyl carbamate and the internal standard, isotopically labeled ethyl carbamate, were generated by plotting the peak heights of the strongest IR bands (1326 cm^{-1} for ethyl carbamate and 1298 cm^{-1} for the internal standard) versus the amount injected over the range of 0.5 to 8.0 ng. The percent relative standard deviations for three to four replicate analyses ranged from 1.3 to 11.8.

Examples were given of the separate determinations of 1.4 and 7.5 ng of ethyl carbamate in two whiskey extracts. In general, the levels of ethyl carbamate in five whiskey extracts as determined by GC/MI-FTIR were in good agreement with those found by GC/MS/MS. This supported the quantification based on GC/MI-FTIR results. However, the authors concluded that, at present, operation of the commercial GC/MI-FTIR system, especially for quantitative measurements, is neither simple nor routine.

V. EXTENSIONS OF CURRENT METHODOLOGY AND RELATED DEVELOPMENTS

With the development of GC/MI-FTIR over the past few years, MI spectrometric techniques have progressed from being purely research tools for the characterization of single species to becoming useful methods for the analysis of complex mixtures. Recent efforts have expanded the use of MI techniques to include (1) the combination of GC and MI-F spectrometry; (2) the combination of other chromatographic techniques, such as supercritical fluid chromatography, and MI-FTIR spectrometry; and (3), in related studies, the development of cryogenic GC/FTIR techniques that circumvent the use of a matrix material. The following is a brief description of these recent advances.

A. Combination of Gas Chromatography and Matrix Isolation Fluorescence Spectrometry

Molecular fluorescence spectrometry is well-suited for use as a GC detector because of its high sensitivity for fluorescent compounds, high selectivity, and fast response. The principal shortcoming of conventional fluorescence GC detectors, which use heated flow cells, is that fluorescence spectra of gases measured at high temperatures are broader and more complex than those measured in the condensed phase. This makes the identification of unknown components difficult. To improve the selectivity of fluorometric GC detectors, Conrad et al. [155] of the University of Tennessee used MI techniques to obtain high-resolution fluorescence spectra of GC eluents.

The cryogenic sampling system used in this study [155] was very similar to the apparatus designed by the same group [122] for GC/MI-FTIR spectrometry, which featured a movable 12-sided deposition surface. The optical system consisted of a xenon lamp whose output was passed through an optical filter and then focused onto the cryogenic deposition surface. The optical filter limited the wavelength range for excitation to 220-345 nm. Fluorescence was collected via right-angle geometry and directed to a grating polychromator, which dispersed the fluorescence spectrum onto a silicon-intensified-target Vidicon detector.

In preliminary tests of the system, no band broadening was observed for spectra of compounds deposited by elution from the GC when they were compared to spectra obtained by using conventional deposition techniques. The absence of band broadening, a sensitive test for aggregation, indicated that true matrix isolation was achieved. A synthetic mixture of 12 anthracene derivatives was separated by the GC and

deposited on four separate mirrored faces of the cryogenic sample collector, which resulted in the deposition of three different compounds on each face. Identification of specific compounds in the respective fractions was based on the presence of two well-defined spectral features not exhibited by any other component; this criterion allowed identification of 11 of the 12 derivatives.

The system was used to determine the pyrene content in three different NBS reference materials. The quantitative results were within 9% of the certified standard values. Analyses of six replicate injections of anthracene yielded a relative standard deviation of approximately 11% in the spectral peak area. The linear dynamic range of the system for PAHs was in excess of three decades; the detection limit for PAHs was approximately 1 ng. The authors pointed out that spectral resolution and sensitivity were sacrificed for speed of operation in this system. The requirement of a GC detector to detect and identify unknown components precludes the use of selective excitation, such as that possible with a tunable laser. Nevertheless, MI-F spectrometry was shown to be a useful GC detector, which could provide information that is complementary to GC/MI-FTIR analytical data.

B. Combination of Other Chromatographic Methods and Matrix Isolation Infrared Spectrometry

One area of increasing interest to analytical chemists is supercritical fluid chromatography (SFC). Often, SFC can be used to separate compounds that have high molecular weights or contain multiple functional groups and cannot be analyzed by GC or LC methods. As with any chromatographic technique, the identification of the separated components is often the ultimate goal. Several workers have developed FTIR interfaces for SFC, which use either a flow cell [156-158], a DRIFT accessory [159, 160], or an FTIR microscope [161, 162] to identify the eluates. Raymer et al. [163] published preliminary results illustrating the combination of capillary SFC and MI-FTIR spectrometry using commercially available instrumentation.

In the SFC/MI-FTIR experiment [163], the effluent from the supercritical fluid chromatograph was split between an FID and a cryogenic collector, as in most GC/MI-FTIR systems. Either CO_2 or CO_2/CCl_4 (99.5/0.5 mol%) was used as the supercritical fluid. To eliminate CO_2 deposition, the cryogenic disk was maintained at 150 K. The matrix material was CCl_4, which is a solid at 150 K, is relatively free of IR absorption above 900 cm^{-1}, and has a minimal effect as a modifier of the CO_2 mobile phase. The CO_2/CCl_4 mobile phase increased the noise and the baseline level of the FID response, although nanogram levels

of analyte could still be detected. An MI-FTIR spectrum of 81 ng of 1,4-naphthoquinone in a CCl_4 matrix exhibited sharp spectral features and a good S/N ratio. However, MI-FTIR spectra of n-octanol exhibited a broad OH stretching band both with and without the CCl_4 matrix, which indicated incomplete matrix isolation of the solute in CCl_4.

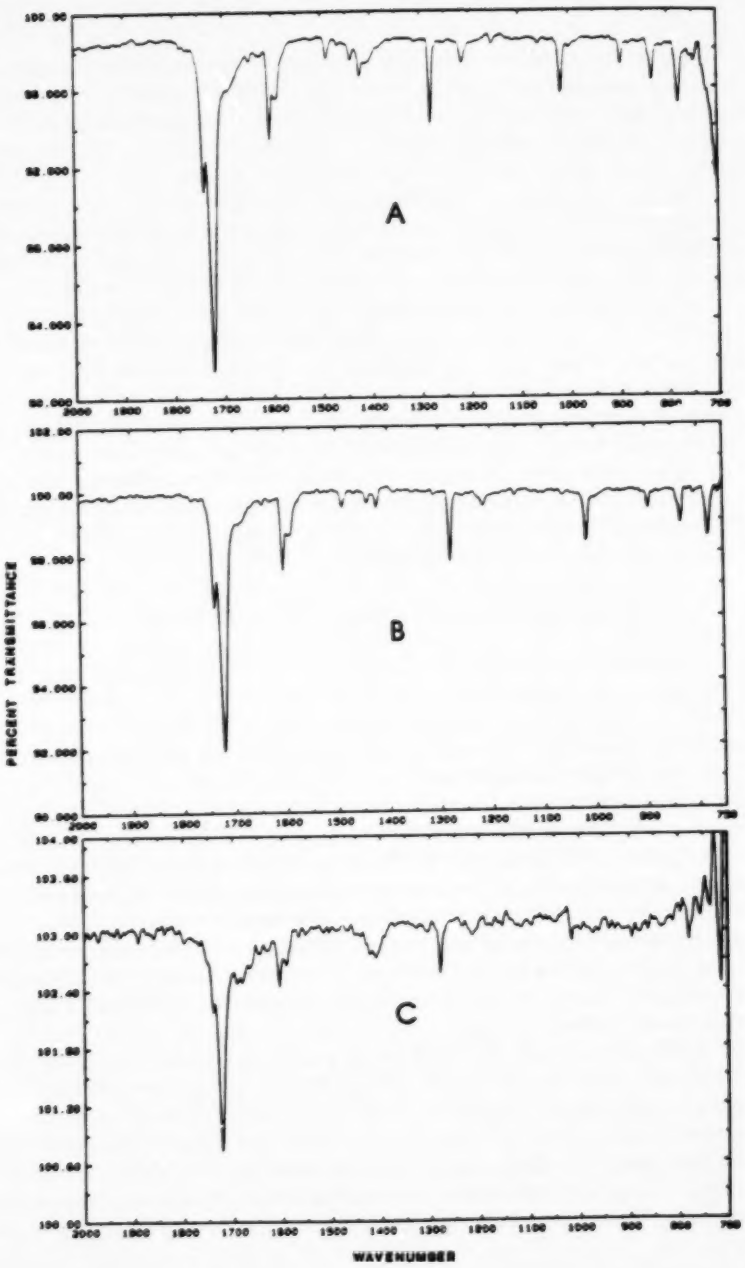
In an extension of capillary gas chromatography, Lee and Warren [164] interfaced a multidimensional gas chromatograph (MDGC) to a Cryolect system and illustrated the capabilities of the system by characterizing hydrocarbons and agricultural chemicals in complex mixtures.

Wehry and Mamantov [88] and Hinton et al. [95] discussed the possibility of using MI-FTIR spectrometry for on-line characterization of LC eluates. However, they noted that for this application to be successful, the solvent must be eliminated before the sample is deposited. Fractional sublimation might be appropriate for this application, provided that the solvent is more volatile than any of the sample constituents of interest. Wehry and Mamantov [88] noted that the approaches used in LC/MS interfaces to eliminate the solvent could also be applied to MI-FTIR spectrometry. However, to our knowledge, no successful LC/MI-FTIR systems have yet been implemented.

C. Other Low-Temperature GC/FTIR Interfaces

Recently, two groups [165-168] independently developed GC/FTIR interfaces that deposit the analyte on a substrate held at subambient temperatures. These interfaces do not mix the GC effluent with matrix gas during deposition; therefore, the analyte is not matrix-isolated. Thus, IR spectra obtained under these conditions do not exhibit the sharp features that are characteristic of MI-IR spectra, but exhibit the broader features of condensed-phase spectra. As a result, some of the molecular specificity gained by obtaining IR spectra under MI conditions is lost. However, the more extensive condensed-phase IR spectral libraries can be searched to identify unknown compounds analyzed under these conditions. These new developments offer a less expensive, less complex alternative to GC/MI-FTIR interfaces. Several advantages, disadvantages, and trade-offs of the low-temperature GC/FTIR interfaces are discussed below.

Shafer et al. [165] designed a GC/FTIR interface in which the analyte was deposited on a stationary KBr window held at ambient temperature. The window was then transferred to an FTIR microscope accessory, and the IR spectrum of the deposited sample was measured. Infrared spectra of high quality were obtained for samples at the low-nanogram level; the minimum identifiable limit for acenaphthenequinone was about 900 pg (see Fig. 9). The authors noted that the key for sensi-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tive GC/FTIR measurements is the ability to contain each analyte in a small cross-sectional area, rather than trapping them in an inert gas matrix. However, the technique described in this report is feasible only for compounds that condense on the KBr window at ambient temperatures.

Based on this preliminary work, Fuoco et al. [166] constructed an interface for real-time GC/FTIR measurements. In this study the GC effluent was split; 40% was directed to an FID, and the remaining 60% was directed through a heated transfer line and sprayed onto a rectangular (39 × 19 × 2 mm) ZnSe window. The ZnSe window was either held at ambient temperature or thermoelectrically cooled to temperatures as low as 228 K. The window was mounted on a translation stage in the focal plane of an FTIR microscope accessory and could be moved slowly during sample deposition. Real-time IR spectra of the deposit were collected every 1.25 s, and chromatograms were reconstructed from the integrated absorbances of specified spectral regions. After sample deposition was completed, the window could be repositioned to obtain IR spectra of specific GC eluents.

For nonvolatile compounds, such as acenaphthenequinone, the IR band absorbances were the same with the window held either at 295 or 263 K. However, this was not the case with more volatile compounds. For example, in the case of nitrobenzene the temperature of the window had to be lowered to 243 K to retard sample loss. Even at 243 K, 4 ng of nitrobenzene evaporated in 4 min. An increase in the transfer line temperature increased the rate of evaporation of nitrobenzene. Comparison of spectra of nitrobenzene deposited at 243 and 228 K indicated that at 228 K the sample was completely crystalline but at 243 K the deposit was in the liquid state. This difference in physical state of the sample had a noticeable effect on the qualitative appearance of the spectra and on the quantitative calibration curves. When the sample was in the crystalline phase, scattering caused band distortions and sloping baselines. Also, during sample deposition when the window was held at subambient temperatures, a portion of the eluent condensed on the deposition tip because of convective cooling caused by the close proximity of the tip to the cold window. In contrast, condensation on the deposition tip is minimized in matrix-isolation GC/FTIR systems by the vacuum surrounding the tip and the cryogenic sample collector.

FIG. 9. GC/FTIR spectra of acenaphthenequinone obtained at ambient temperatures for injected quantities of (A) 3.5 ng, (B) 1.7 ng, and (C) 900 pg; 64 scans were averaged for each spectrum. Reprinted from Ref. 165. Copyright 1986 by Dr. Alfred Huethig Publishers.

The FID response and the IR reconstruction of a chromatogram obtained from a mixture of p-nitrophenol, 2,4-dinitrotoluene, and 4,6-dinitro-o-cresol exhibited almost identical resolution, which indicated that the separation achieved by the capillary column was maintained by the interface. The utility of the interface was illustrated by analyzing a standard environmental reference mixture of neutral extractables. Identifiable spectra of most compounds in the mixture were obtained for 7 ng of each component delivered to the interface. However, o-dichlorobenzene evaporated too quickly and benzo[k]fluoranthene was too weakly IR-absorbing to allow identification at this level. For this analysis the transfer line temperature had to be adjusted to coincide with the oven temperature to avoid premature evaporation of the more volatile components.

Sensitivity of this interface was not quite as high as that of the Cryolect system, but was approximately an order of magnitude better than with the light-pipe interface. Detection limits for molecules of low volatility and high IR absorptivities were approximately 100 pg; the minimum amount of sample needed for identification was 500 pg.

This GC/FTIR interface design was improved to allow GC eluents to be trapped on a moveable ZnSe window that was enclosed in an evacuated chamber and cooled to 77 K with liquid nitrogen [167]. This design eliminated many of the problems with the original system, such as evaporation of volatile compounds from the deposition surface and condensation of nonvolatile compounds on the deposition tip. The new design also reduced the spot size of the deposit to approximately 100 μm, which is slightly less than one-half of the width measured in the previous studies [165, 166]. The ability to match the spot size with the area of the detector element increased the sensitivity of the system. For instance, an identifiable spectrum of 4 ng of diisobutyl phthalate was obtained in "pseudo-real time," that is, as the sample passed through the IR beam a short time after deposition. Subnanogram (400 pg) levels of diisobutyl phthalate could be detected in this manner. In future developments the authors predicted a fourfold reduction in noise level and minimum identifiable quantities of less than 100 pg for pseudo-real-time measurements of polar compounds by using this type of GC/FTIR system.

Brown and Wilkins [168] designed a cryogenically cooled interface to collect effluents directly from a capillary GC without incorporating the separated components into a frozen matrix. The interface used a liquid nitrogen-filled Dewar to cool the sample collector, which significantly reduced costs from that required for systems that use a closed-cycle helium refrigerator. The Dewar can be maintained at 77 K for 16 h with a single fill of liquid nitrogen. The temperature of the Dewar

can be lowered to 65 K, the triple point of nitrogen, by attaching a mechanical pump to the Dewar exhaust and maintaining a pressure of about 1.3×10^{-2} kPa. Other than the method for cooling the sample collector, the interface was similar to the GC/MI-FTIR system developed by Reedy and coworkers [124]. The sample collector was a gold-coated copper disk, 2.54 cm thick and 10.16 cm in diameter. The disk

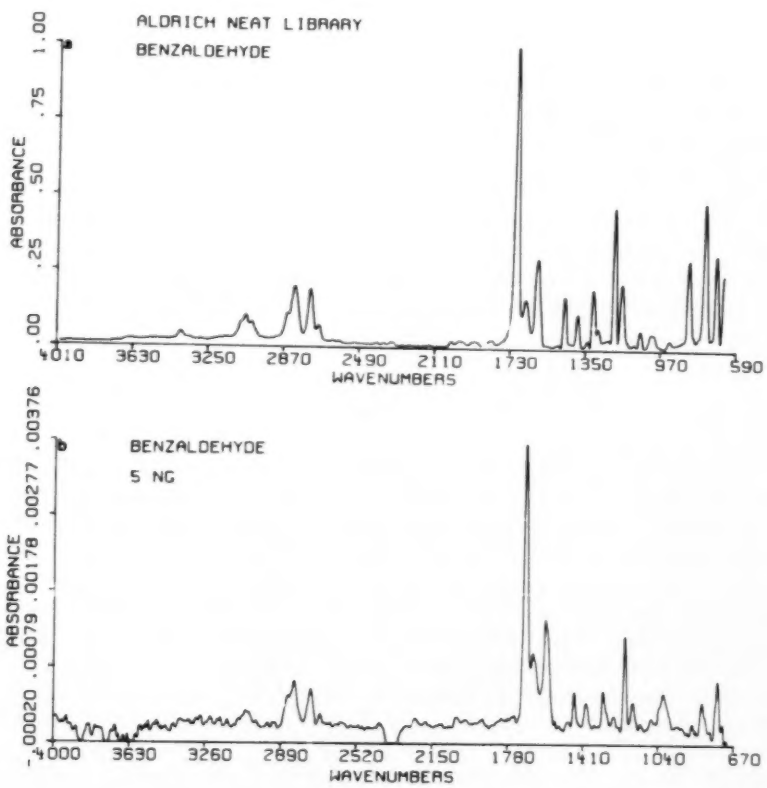

FIG. 10. (a) Reference library spectrum of neat benzaldehyde from Aldrich spectral library. (b) GC/FTIR spectrum of benzaldehyde (5 ng) obtained at 77 K. Reprinted from Ref. 168. Copyright 1988 by American Chemical Society.

can be rotated continuously by a computer-controlled stepper motor. The disk was large enough to collect approximately 7.5 h of chromatographic effluent. The IR beam was focused onto the sample by a parabolic reflector, collected by another parabolic reflector, and then directed to an MCT detector. The position of the deposition tip, which was attached to a heated transfer line interfaced to the GC, could be viewed through a binocular microscope. Sample losses due to volatilization were minimal at 77 K for a typical compound, benzaldehyde. The IR response of the system was linear for benzaldehyde from 1 to 30 ng. The IR spectrum of benzaldehyde obtained at 77 K was comparable to a neat, room-temperature reference spectrum and could be identified by searching a condensed-phase IR library (see Fig. 10). A quality IR spectrum of 1 ng of nonane was obtained, which led the authors to conclude that subnanogram quantities could be detected and identified with this GC/FTIR system. This interface was also used to collect matrix-isolated IR spectra of GC effluents by lowering the temperature of the Dewar to 65 K and mixing 1% xenon postcolumn in the carrier gas stream. The matrix-isolated IR spectrum of benzaldehyde was approximately three times as intense as the nonmatrix-isolated spectrum and exhibited much sharper bandwidths. However, under the conditions of the experiment, approximately 50% of the xenon was lost after 3 h.

VI. SUMMARY

The illustrations discussed in this review demonstrate that MI-FTIR spectrometry is rapidly developing as a useful analytical technique for detecting and identifying trace quantities of unknown components in complex mixtures. Because of its enhanced sensitivity and its freedom from many of the chromatographic constraints that limit other IR techniques, MI-FTIR spectrometry can be used in conjunction with a variety of separation methods, such as capillary GC, multidimensional GC and SFC. A GC/MI-FTIR system can also be interfaced to other analytical systems, such as a mass spectrometer or fluorescence spectrometer, to obtain complementary spectral information from a single sample injection. These advantages, along with an increasing understanding of the factors that influence the characteristics of MI-FTIR spectra, promise to promote a rapid expansion of MI-FTIR applications in the future.

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Disclaimer

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ABBREVIATIONS USED

ATR	attenuated total reflectance
DRIFT	diffuse reflectance infrared Fourier transform
FID	flame ionization detector
FTIR	Fourier transform infrared (spectrometry)
FWHH	full width at half height
GC	gas chromatography
HPLC	high performance liquid chromatography
LC	liquid chromatography
MCT	mercury-cadmium telluride
MDGC	multidimensional gas chromatography
MI	matrix isolation
MS	mass spectrometry
M/S	matrix-to-solute
NBS	National Bureau of Standards
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PD	pulsed deposition
SFC	supercritical fluid chromatography
S/N	signal-to-noise
SS	solid state/solution
SSO	slow spray-on deposition
TCDD	tetrachlorodibenzo-p-dioxin
TCDF	tetrachlorodibenzofuran
UV	ultraviolet
VP	vapor phase

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